Radically New Adsorption Cycles for Carbon Dioxide Sequestration

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Introduction

- It is generally accepted that the increasing global temperatures over recent decades are due to increasing atmospheric concentrations of greenhouse gases, i.e., CH_4, N_2O, and particularly CO_2.
- The idea of carbon sequestration is probably the newest means being studied to manage CO_2 in the environment.
- The most likely options for CO_2 sequestration are
  - chemical and physical absorption
  - low-temperature distillation
  - gas separation membranes and
  - physical and chemical adsorption

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  - gas separation membranes and
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Currently absorption is the most widely deployed commercial technology, but it requires significant amount of heat for solvent regeneration.

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Cryogenic distillation is certainly feasible and widely practiced for CO_2 recovery, but only viable for CO_2 concentrations higher that 90 vol%, which is outside the range for flue gas streams.

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Polymeric, ceramic and metallic membranes are all viable for CO_2 recovery from flue gas streams; however, each have their own issues involving low fluxes, degradation, fouling, cost, etc.

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  - **low-temperature distillation**
  - **gas separation membranes and**
  - **physical and chemical adsorption.**

Various adsorption processes for concentrating CO_2 from flue gas streams have been proposed and explored, with many of the results being controversial and a breakthrough being sought.

Overall Objectives

- Propose why adsorption technology still has potential for CO_2 separation and capture
- Introduce new adsorption cycle concepts that mimic distillation technology
- Introduce new adsorbent material for reversible CO_2 adsorption at high temperature
- Describe high temperature adsorption cycles for concentrating CO_2 from stack and flue gases
- Provide convincing evidence that further justifies study of high temperature adsorption cycles
- Elaborate on industrial and government agency collaborations to strengthen possibility of success

Overall Objectives

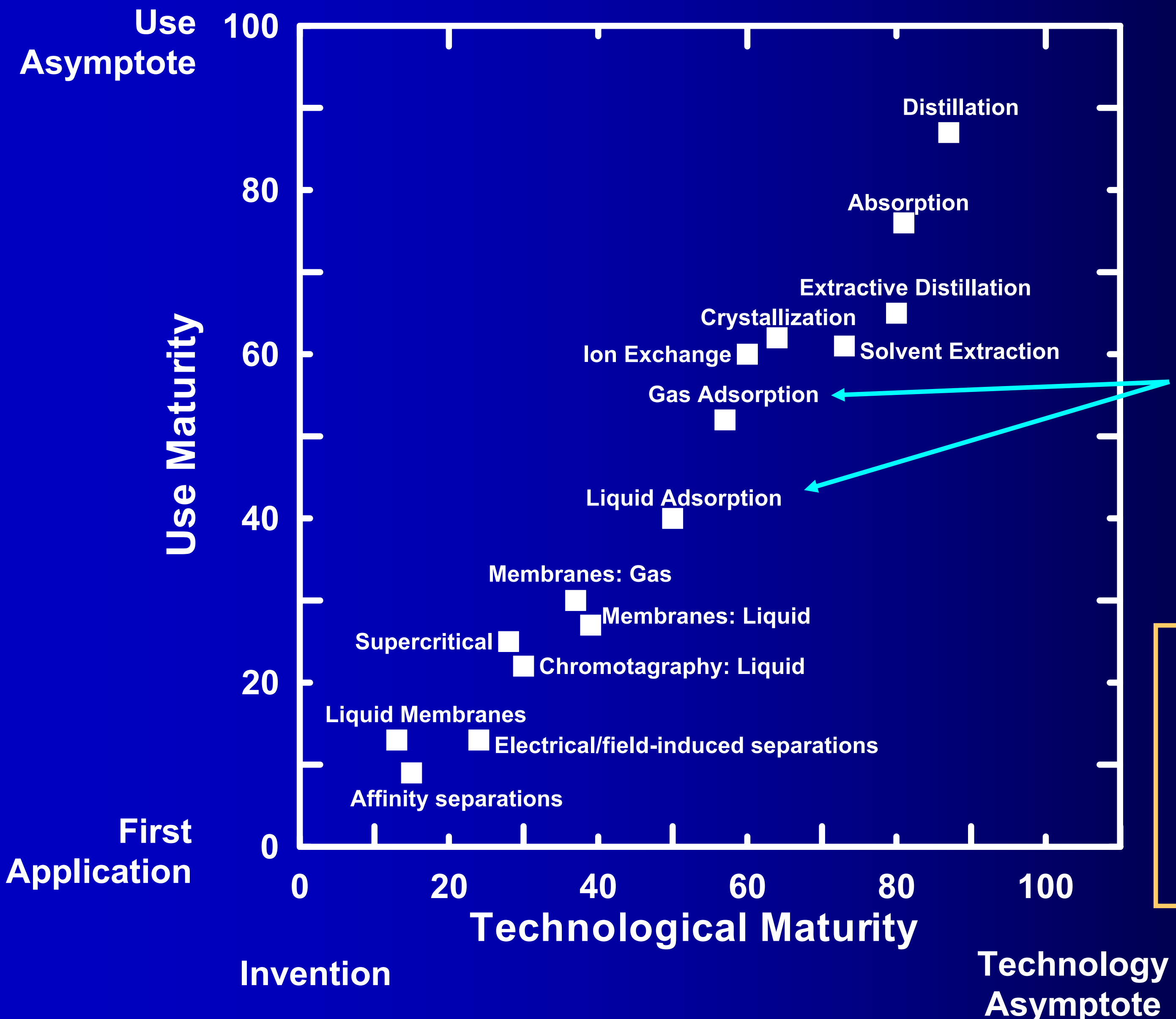
- Propose why adsorption technology still has potential for CO_2 separation and capture

Why does adsorption have potential?

- extra degree of thermodynamic freedom compared to e.g., distillation and absorption, due to the presence of the adsorbent
- many different families of porous adsorbents available, new and old, which offer a vast array of equilibrium, kinetic and energetic properties
- many possible pathways (i.e., different combinations of materials and processes) that achieve the same separation performance
- unique match often found between optimum adsorbent and efficient process design

These are key driving forces that promote innovation and breakthroughs.

Separation Process Maturity



Adsorption technology centrally located on this graph, what does this mean?

There is still a great deal of potential!

Adsorption Technology

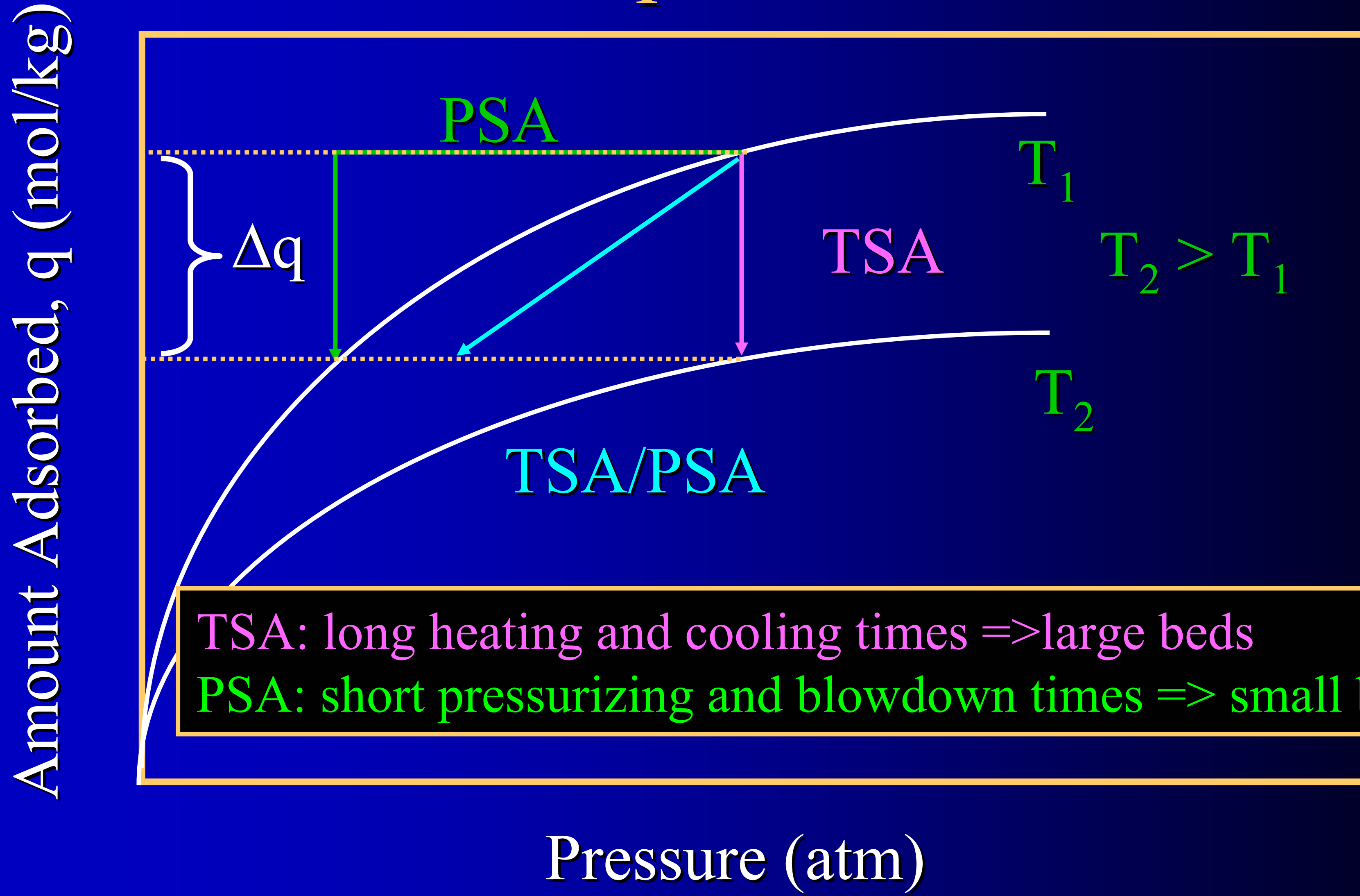
Commercial Regeneration Schemes

- pressure swing adsorption
- displacement purge
- thermal swing adsorption
- steam regeneration

Classic Commercial Process Modes

- fixed bed
- rotary bed or valve
- simulated moving bed
- moving bed

PSA and TSA Concepts Based on the Adsorption Isotherm



TSA: long heating and cooling times =>large beds

PSA: short pressurizing and blowdown times => small beds

Traditional PSA Cycle Steps

- six basic steps for conventional PSA
  - pressurization with feed or light product
  - high pressure feed with light product production
  - depressurization or blowdown (cocurrent or countercurrent to the feed)
  - desorption at low pressure with light product purge (light reflux), evacuation or both
  - pressure equalization between beds
  - high pressure rinse with heavy product (purge or heavy reflux) following feed

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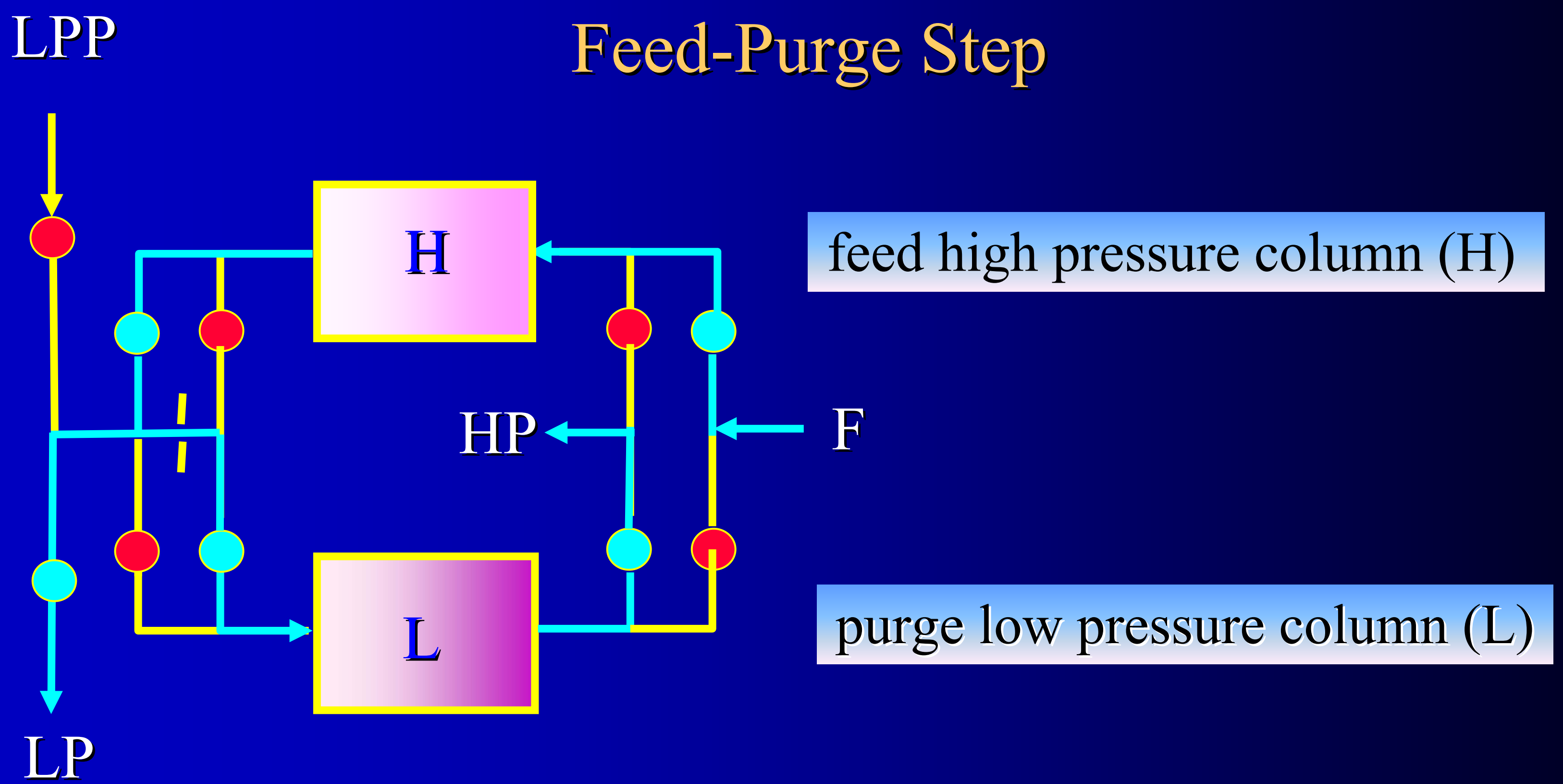
New PSA Cycle Concepts

- enriching reflux (ER) or heavy reflux PSA cycle for producing pure heavy component
- dual reflux (DR) PSA cycle for producing two pure products
- contrast with conventional PSA or stripping reflux (SR) cycle; always designed for producing pure light component

These new PSA cycle concepts mimic distillation technology and hence provide considerably more flexibility to the six traditional cycle steps.

Stripping Reflux PSA

Feed-Purge Step



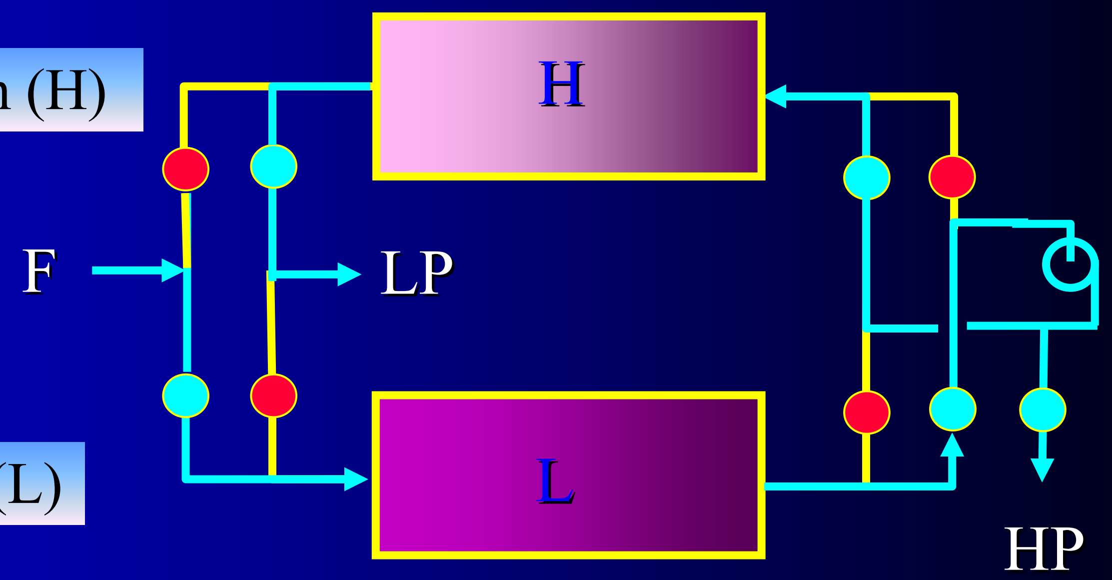
- pure light product (LP) produced
- enriched heavy product (HP) produced, but with $y_{HP}/y_F < P_H/P_L$

Enriching Reflux PSA

Purge-Feed Step

purge high pressure column (H)

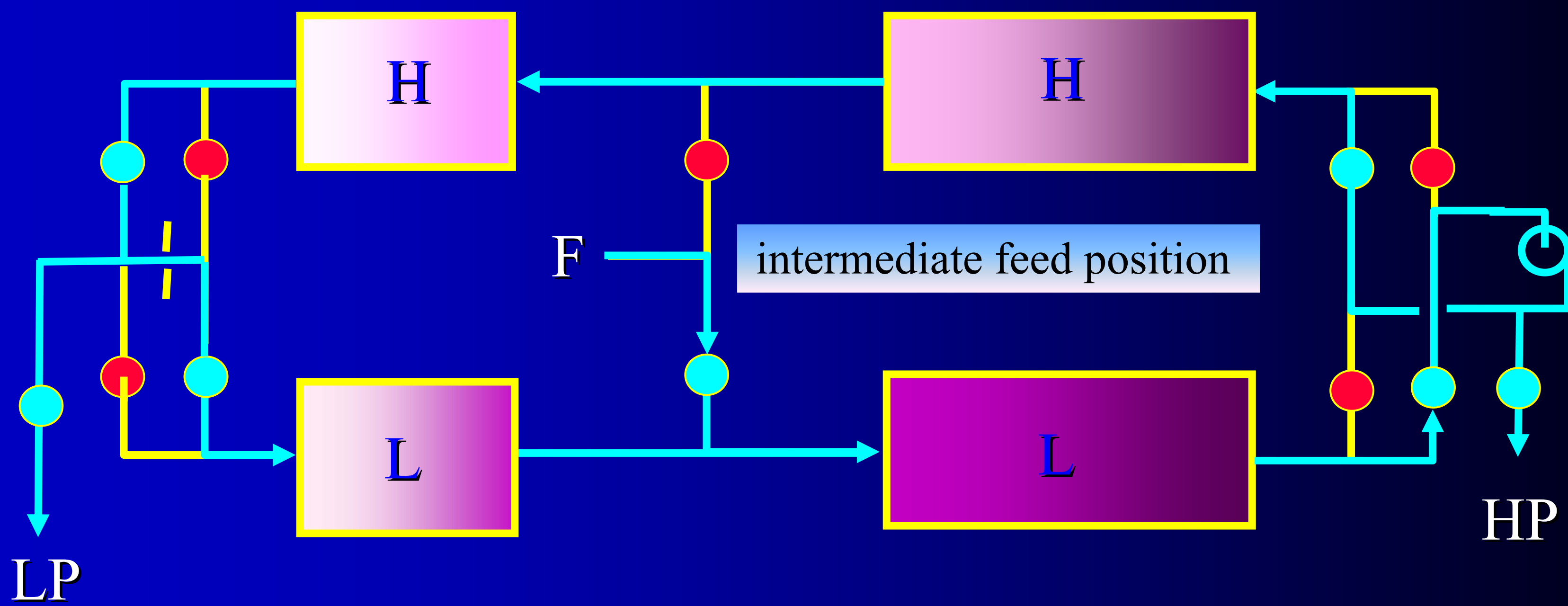
feed low pressure column (L)



- pure heavy product (HP) produced
- light product (LP) produced, but with $y_{LP}/y_F < P_L/P_H$

Dual Reflux PSA

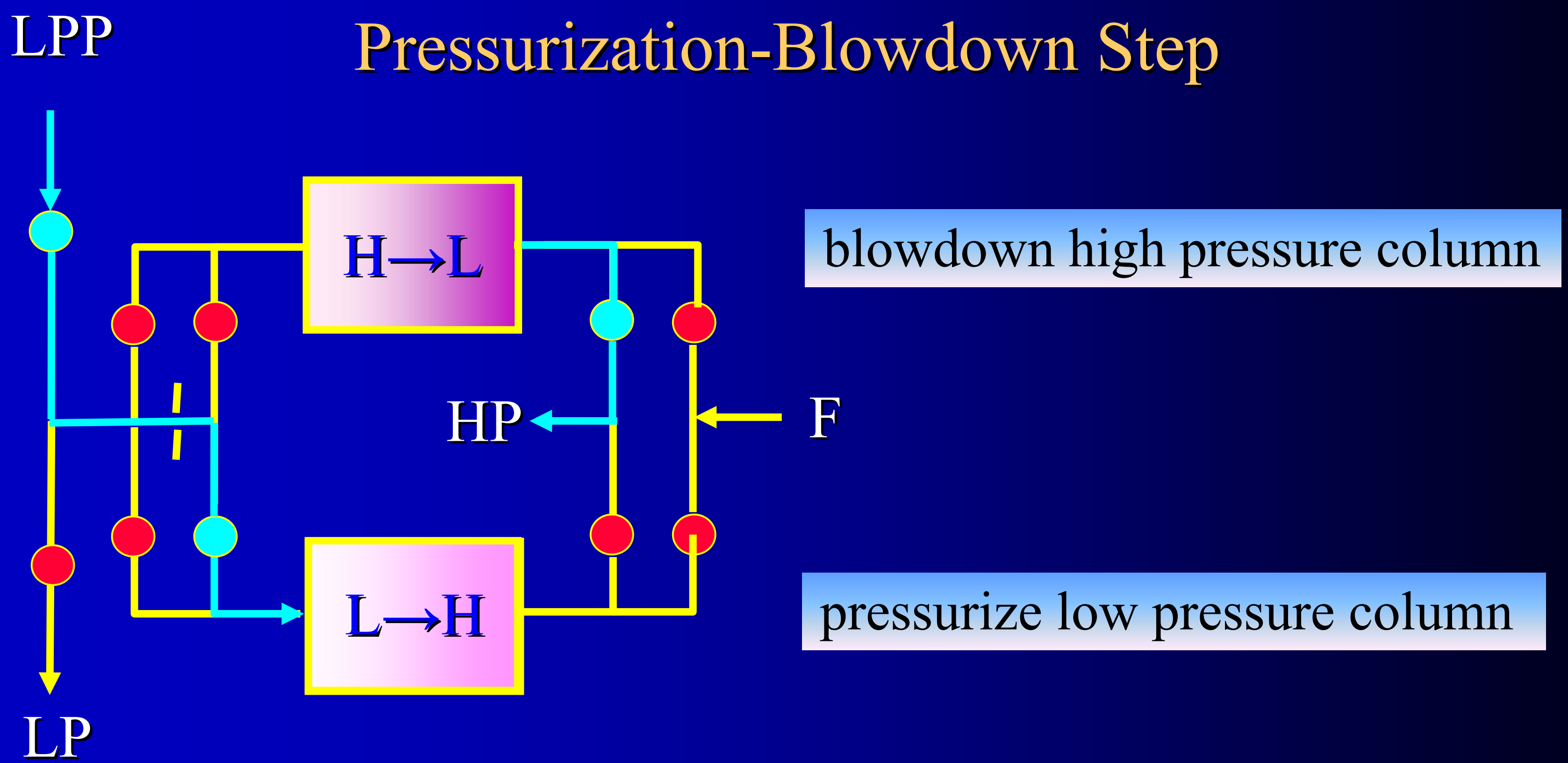
Feed-Purge Step



- feed low pressure, purge low and high pressure columns
- pure heavy product (HP) produced
- pure light product (LP) produced

Stripping Reflux PSA

Pressurization-Blowdown Step



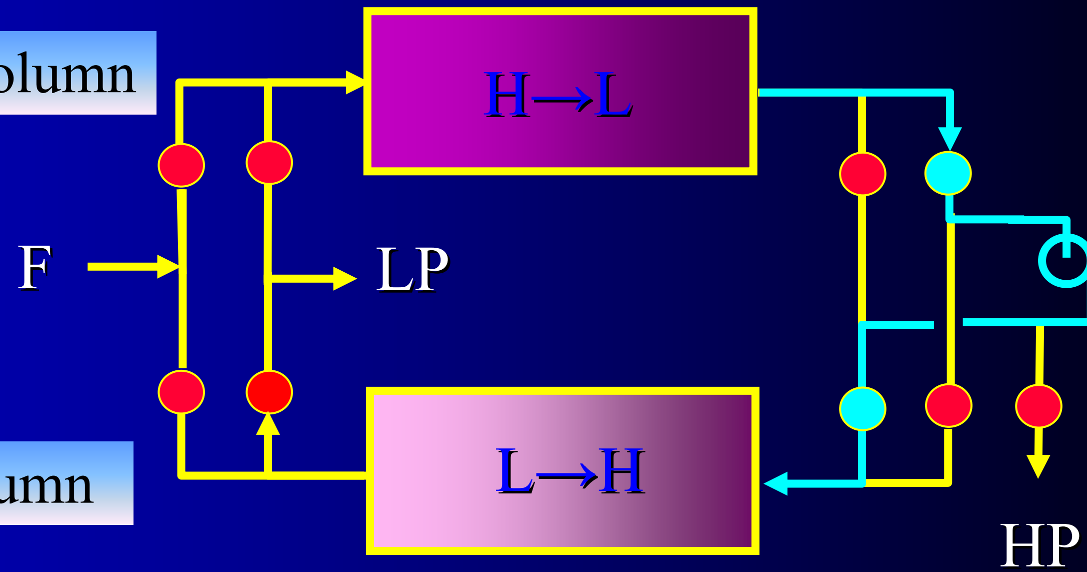
- pure light product used for pressurization (LLP)
- enriched heavy product (HP) produced, but with $y_{HP}/y_F < P_H/P_L$

Enriching Reflux PSA

Blowdown-Pressurization Step

blowdown high pressure column

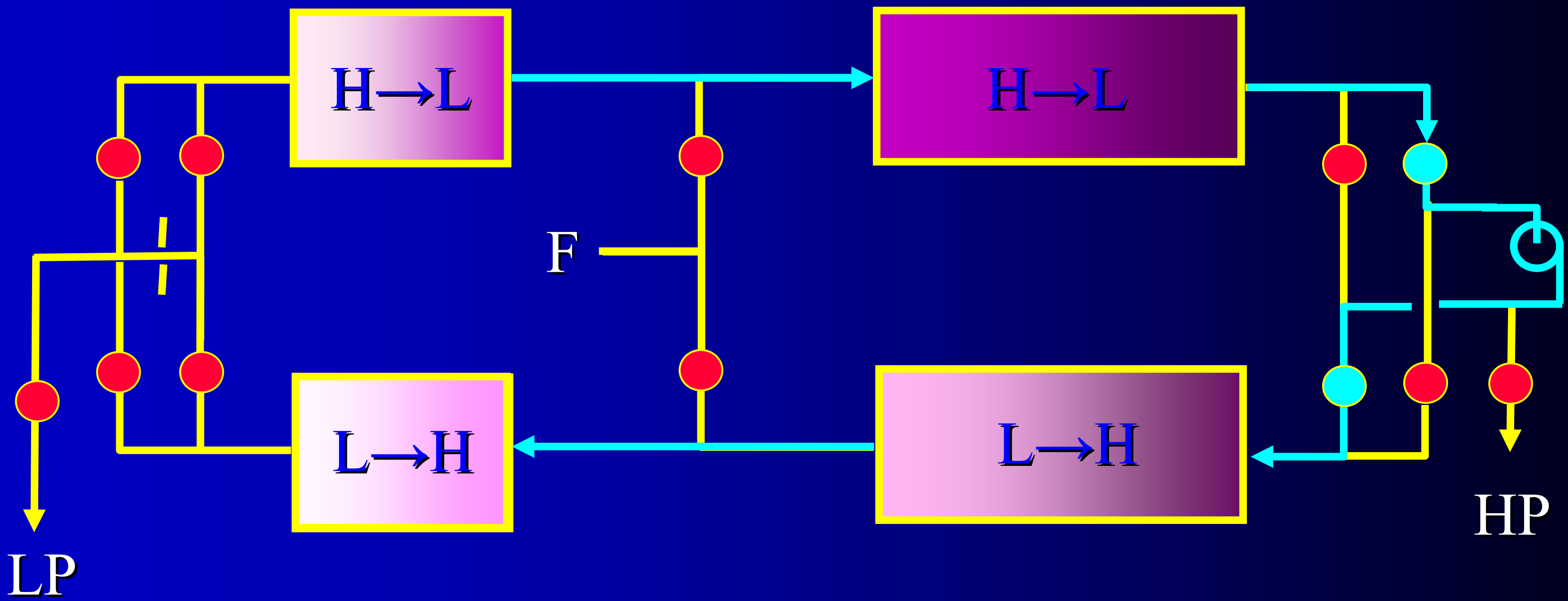
pressurze low pressure column



- enriched gas from high pressure column used to completely pressurize low pressure column
- no products produced

Dual Reflux PSA

Pressurization-Blowdown Step



- enriched gas from high pressure column used to completely pressurize low pressure column
- no products produced

Adsorbent Technology

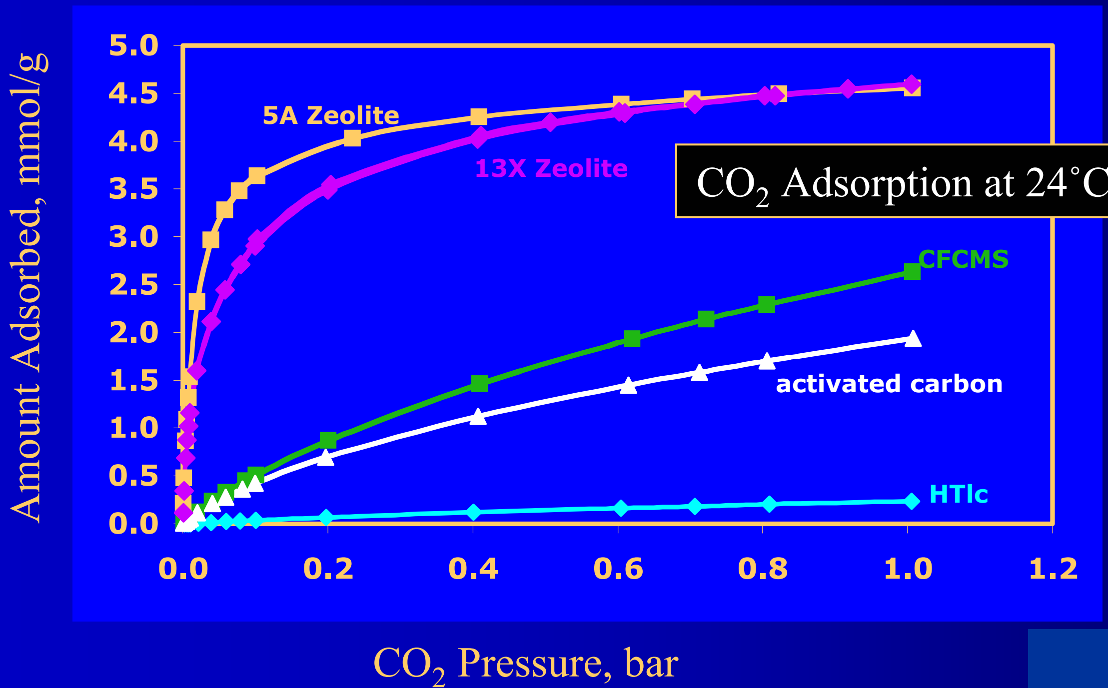
Classic Commercial Adsorbents

- activated carbons
- molecular sieve zeolites
- carbon molecular sieves
- silica gels
- activated aluminas
- ion exchange resins

Newer Commercial Adsorbents

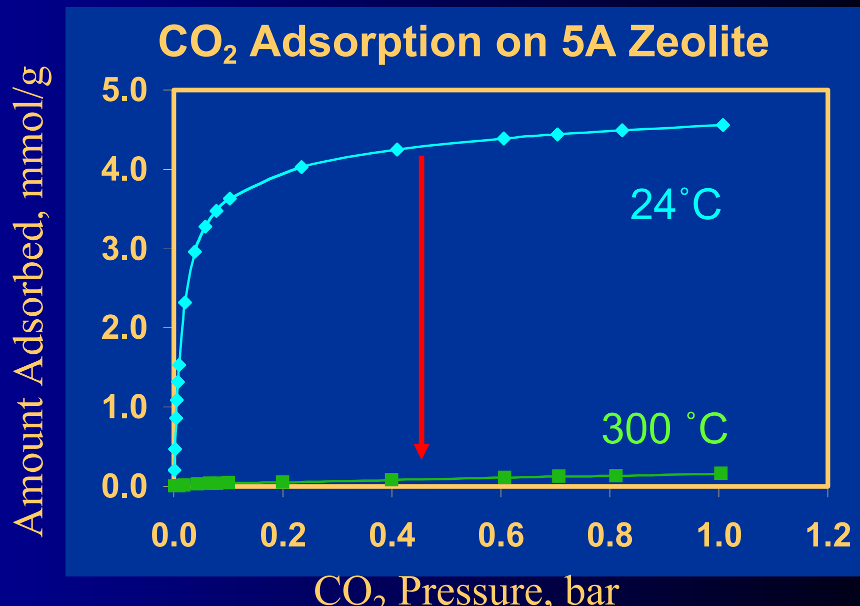
- polymeric
- Π-complexation

Adsorption of CO_2 on Solid Sorbents



Many commonly used adsorbents (e.g., zeolites, activated carbon, carbon MS) have good CO_2 capacity at room temperature.

Typically, CO_2 capacity greatly diminished at elevated temperatures.



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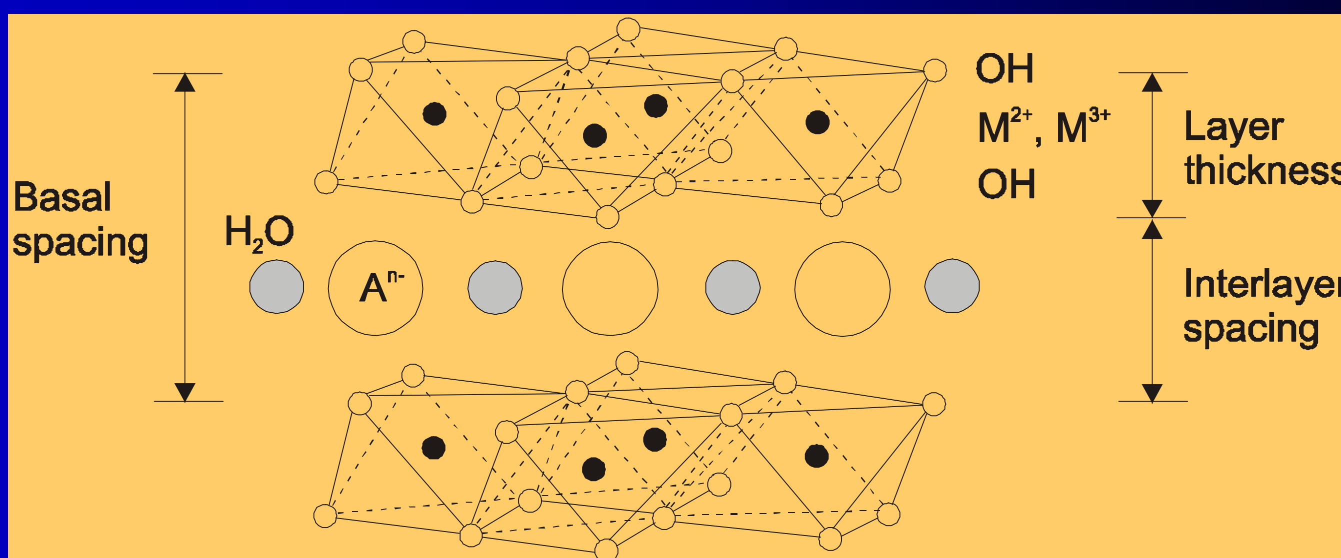
- Introduce new adsorbent material for reversible CO_2 adsorption at high temperature

Hydrotalcite-Like Compound (HTlc) for Reversible CO_2 Adsorption

- also known as layered double hydroxides (LDHs)
- anionic clays (bi-dimensional basic solids)
- used … nts
  and … es,
  and i…
- struc … ith
  inter … ng
  anio…

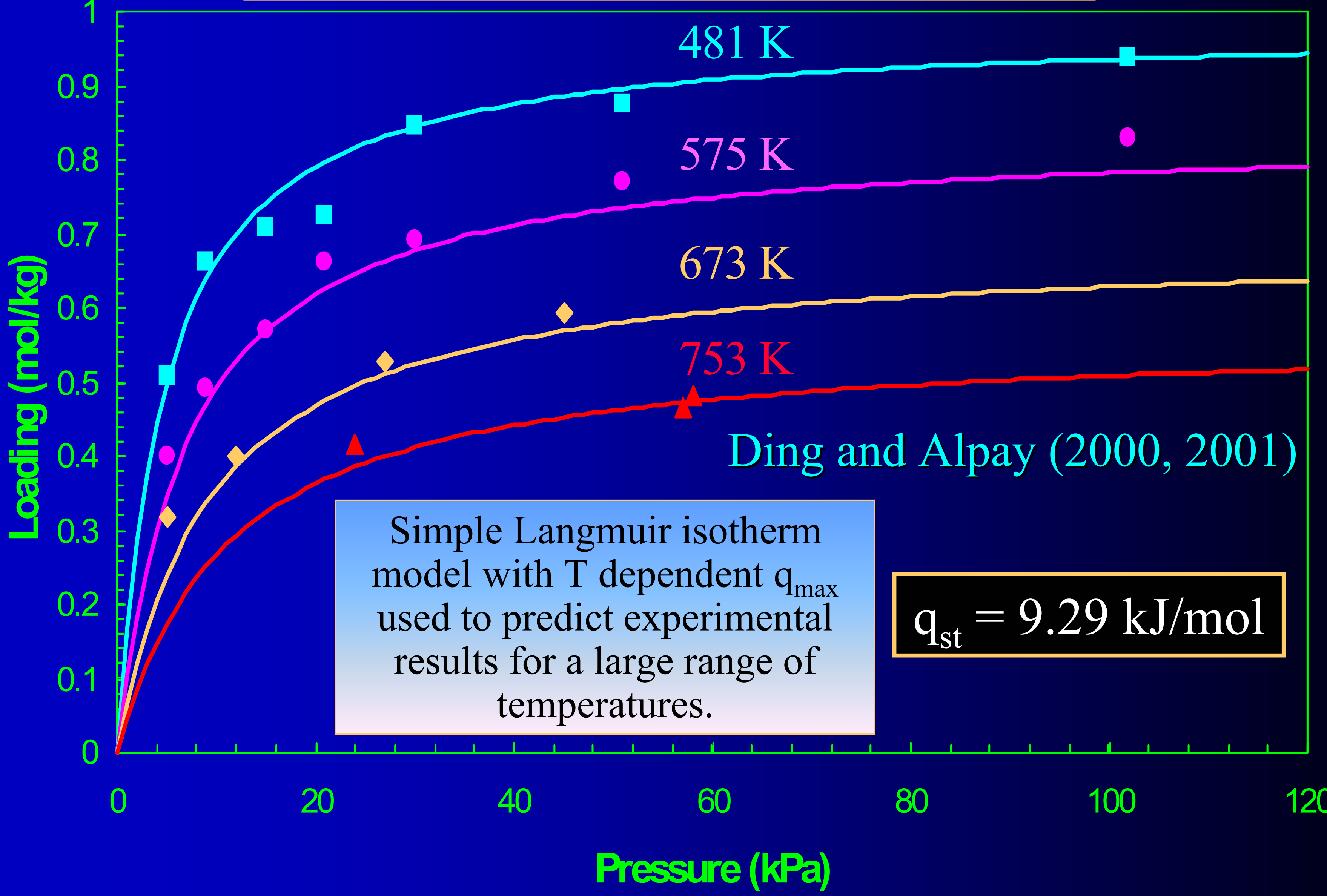
$$[Mg_{0.73}Al_{0.27}(OH)_2](CO_3)_{0.135}\bullet mH_2O$$

$$\left.\begin{array}{l}\text{layer thickness} \approx 4.8\ \text{Å} \\ \text{interlayer spacing} \approx 3.0\ \text{Å} \\ \text{basal spacing} \approx 7.8\ \text{Å}\end{array}\right\}\ \text{unheated}$$



CO_2 Adsorption Isotherms on Hydrotalcite (HTlc)

$[Mg_{0.73}Al_{0.27}(OH)_2](CO_3)_{0.135} \bullet MH_2O$



Simple Langmuir isotherm model with T dependent q_{max} used to predict experimental results for a large range of temperatures.

$q_{st} = 9.29$ kJ/mol

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- Describe high temperature adsorption cycles for concentrating CO_2 from stack and flue gases

High Temperature SR PSA Cycle

- Skarstrom-type, 4-step, vacuum swing cycle operated at 575 K
- based on use of K-promoted HTlc adsorbent selective only for CO_2 and water insensitive
- typical stack gas or flue gas effluent treated
  - obviates need to cool, dry or pressurize the feed stream
  - potential to produce an enriched stream of CO_2 at high recovery

Results obtained from non-linear, isothermal equilibrium theory (NL-IET), and non-isothermal mass transfer limited (NI-MTL) modeling studies.

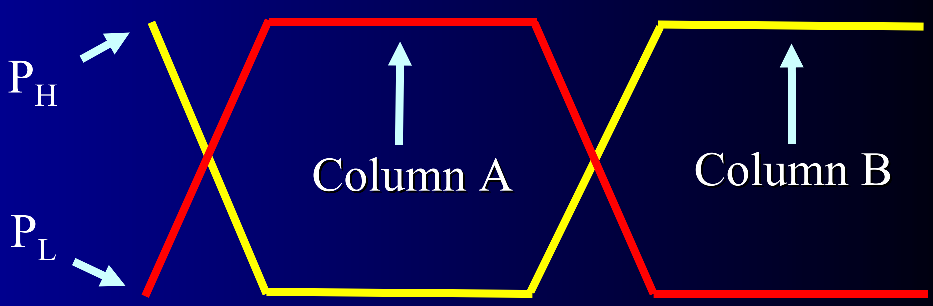
Stripping Reflux (SR) PSA Cycle

- typical 4-step Skarstrom type SR PSA cycle
- countercurrent blowdown and light product pressurization
- many other SR PSA cycle configurations exist
- high purity light product produced

Bed	cyc step	cyc step	cyc step	cyc step
1	high P feed	Cnt-C BD	low P purge	LP pres
2	LP pres	high P feed	Cnt-C BD	low P purge
3	low P purge	LP pres	high P feed	Cnt-C BD
4	Cnt-C BD	low P purge	LP pres	high P feed

LP pres: light product pressurization
high P feed: high pressure feed
Cnt-C BD: countercurrent blowdown
low P purge: low pressure purge

Pressure History of Both Columns



Bed Characteristics, Adsorbent Properties, and Transport Properties

Ding and Alpay (2000, 2001); Liu et al. (1998)

Bed Dimensions and Operating Conditions	L_b (m)	0.2724
	r_b (m)	0.0387
	Q_F (SLPM)	2.0
	T_F, T_o (K)	575
Adsorbent Properties	ε_b	0. 48
	ρ_p (kg/m^3)	1563
	r_p (m)	1.375×10^{-3}
	$C_{p,s}$ (kJ/kg/K)	0.850
Heat and Mass Transfer Coefficients	h_b (kW/m^2/K)	0.00067
	$k_{CO2,ad}$ (s^{-1})	0.0058
	$k_{CO2,de}$ (s^{-1})	0.0006

Different Mass Transfer Rate Constants for Adsorption and Desorption

Non-Linear, Isothermal ET Model of SR PSA

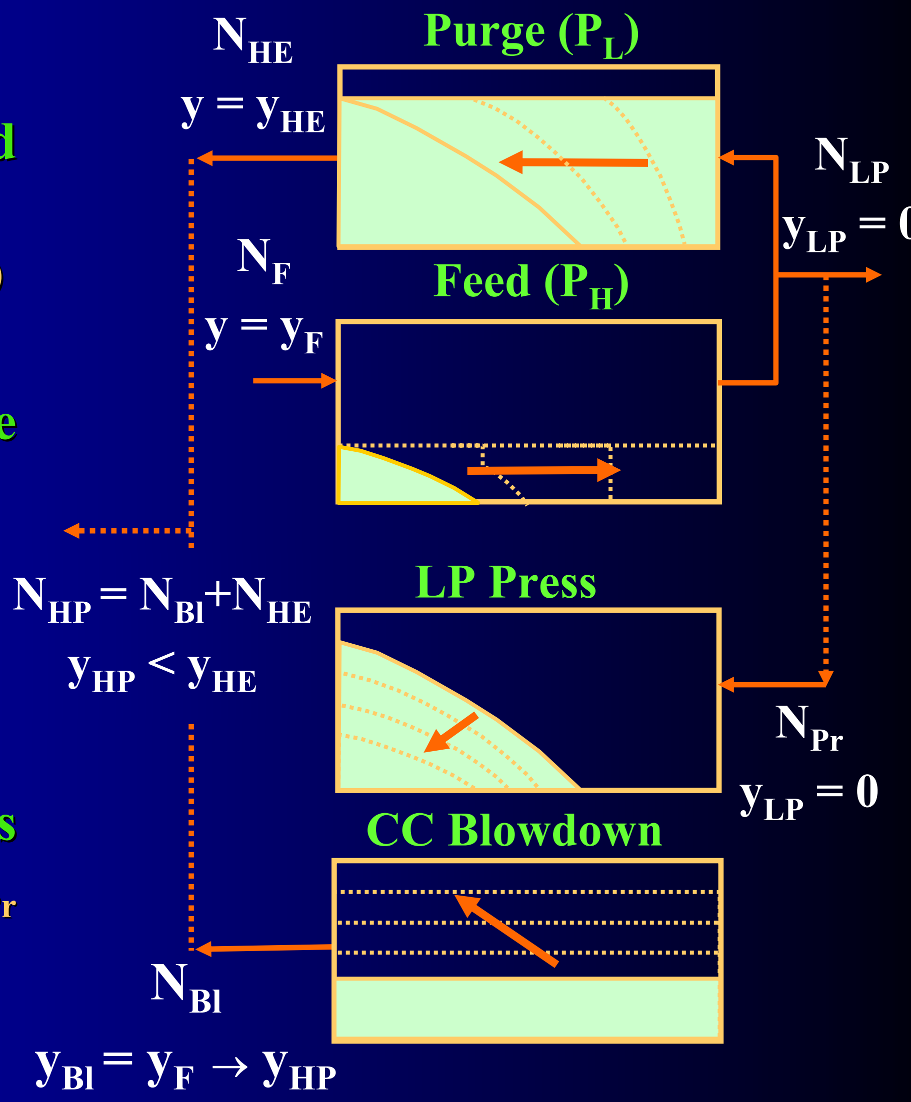
Light Product Pressurization and CounterCurrent Blowdown

ASSUMPTIONS:

- $y = y_F$ CO_2 front in high pressure feed step stops just before breakthrough:
  - →no CO_2 in N_{LP} (i.e., 100% RECOVERY)
  - →homogeneous y along bed in blowdown
- $y = y_{HE}$ CO_2 front in low pressure purge step stops just before breakthrough
- N_{HP} comprises N_{HE} and N_{Bl}
  - → $y_{HP} < y_{HE}$

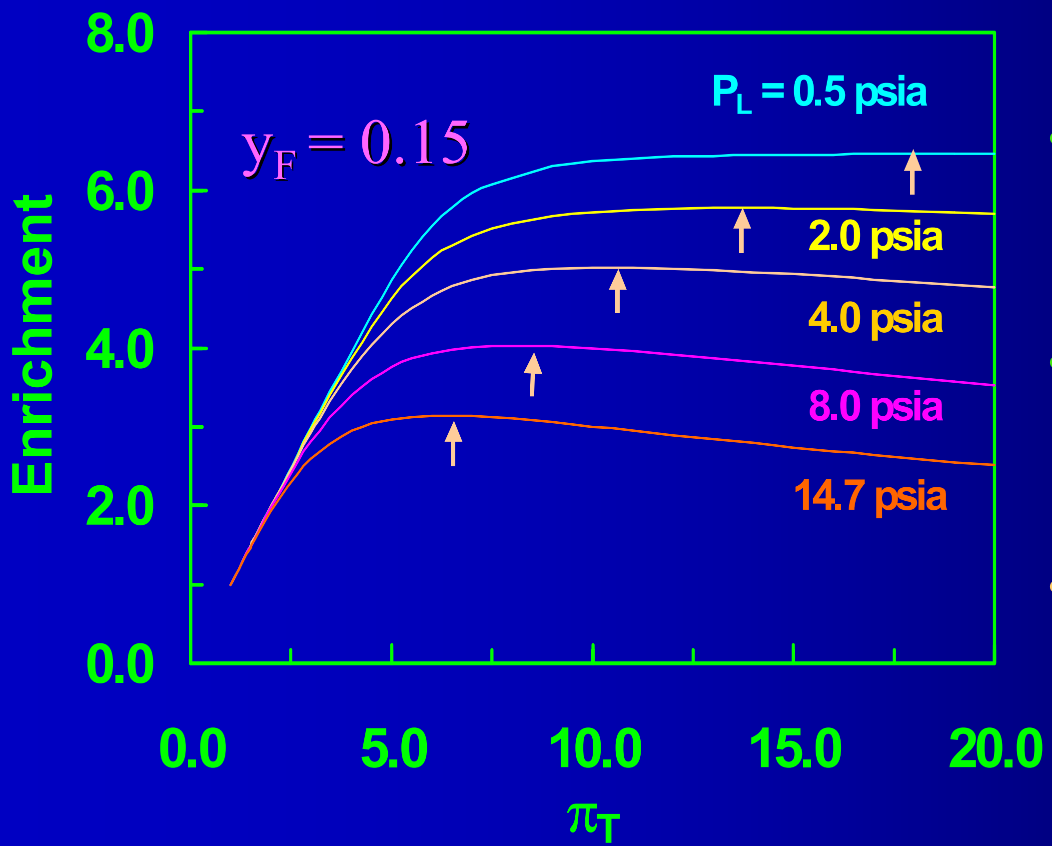
SOLUTION PROCEDURE:

- overall and inert partial balances simultaneously satisfied: solving for N_{Pr} and γ and using equations in literature



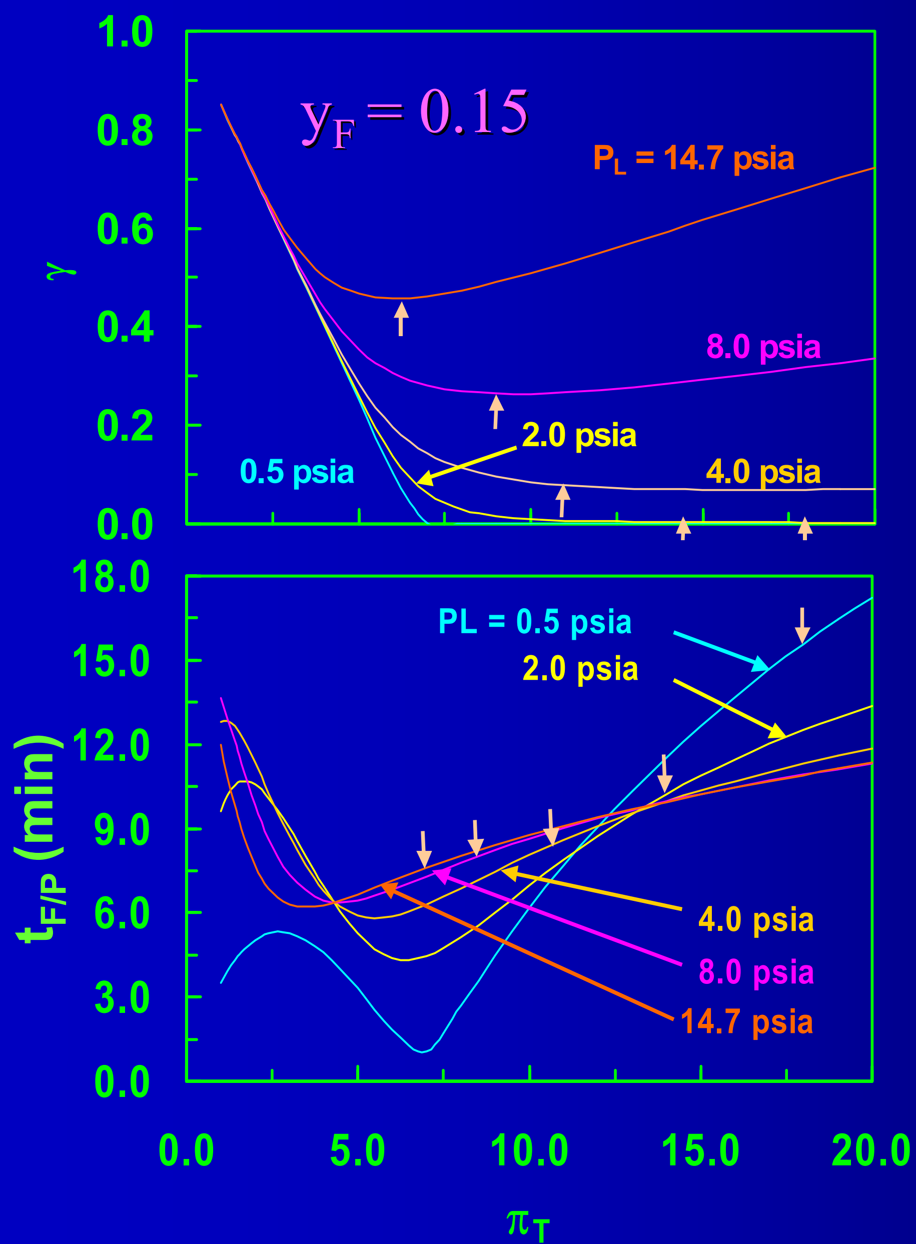
Results of the NLIET SR PSA Model

Effect of the Pressure Ratio (P_H/P_L) and P_L on the CO_2 Enrichment



- Enrichments increase with increasing π_T, but only up to a maximum (indicated by orange arrows)
- Further decrease of enrichments due to diluting role of blowdown in enriched product.
- Thus, ET is helpful in determining qualitative optimum conditions (optimum π_T for given P_L)
- Lower P_L improves the working capacity of the HTlcs and hence better enrichments can be achieved

Results of the NLIET SR PSA Model



Effect of Pressure Ratio (P_H/P_L) and (P_L) on Purge-to-Feed Ratio (γ) and Constant Pressure Step Time ($t_{F/P}$)

- **Besides π_T, ET also provides the purge to feed ratios (γ) and constant pressure step time $t_{F/P}$ (again indicated by arrows) at optimum conditions for given P_L**

- **ET predicts that for smaller P_L, smaller γ and larger $t_{F/P}$ should be used, a consequence of 100 % recoveries always being achieved**

NI-MTL SR PSA Model Assumptions

ASSUMPTIONS:

- ideal gas law
- plug-flow (negligible radial gradients)
- negligible pressure drop
- finite heat and mass transfer resistances
- mass transfer governed by linear driving force approximation
- heat transfer governed by overall heat transfer coefficient
- loading dependent heat of adsorption
- gas and adsorbed phase heat capacities equal and temperature dependent
- constant adsorbent heat capacity

SOLUTION PROCEDURE:

- **unlike ET, optimum conditions can only be found through parametric studies**
- **FORTRAN based numerical code (method of lines) used (DDASPK)**

Rigorous Model!

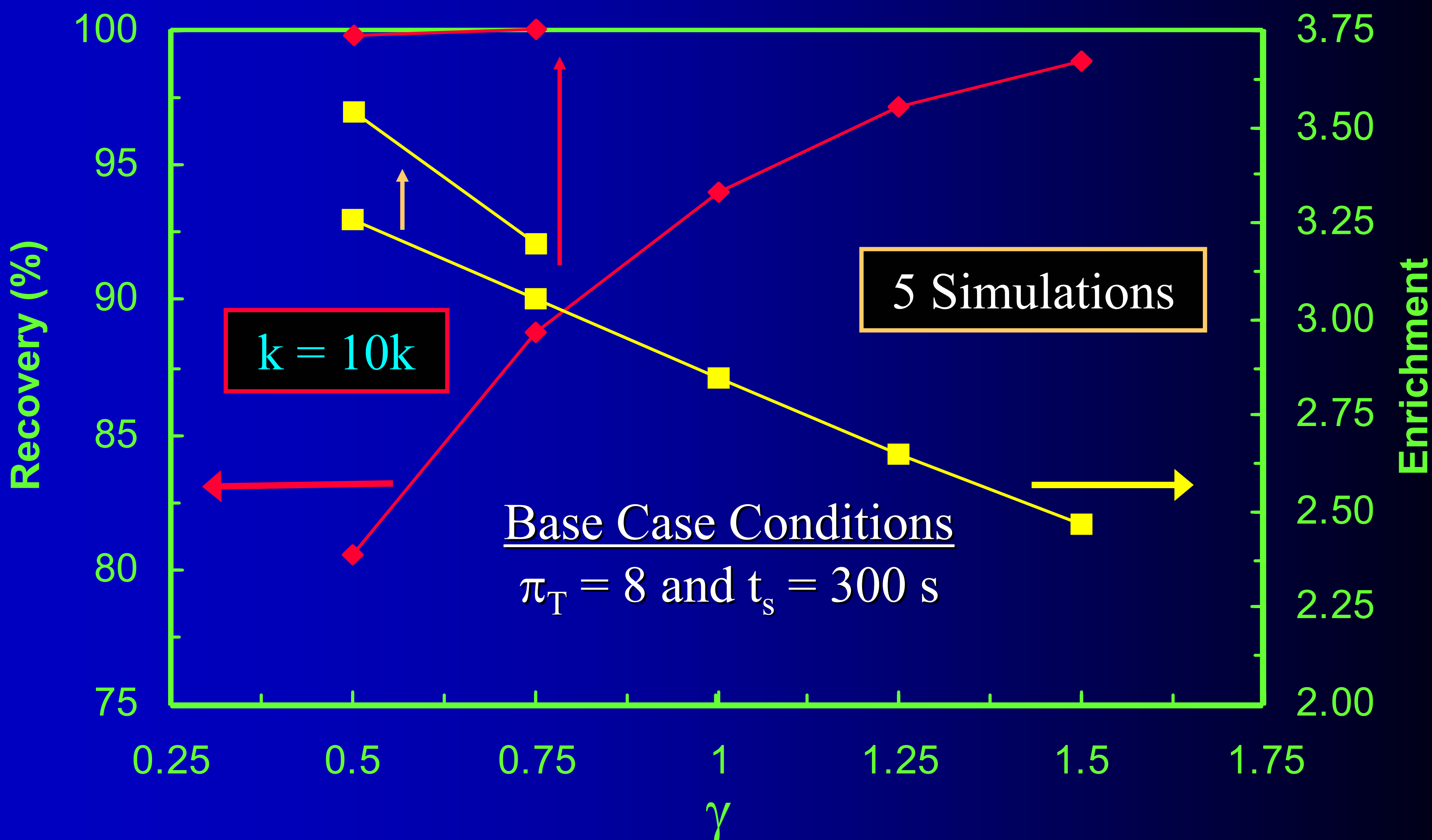
Fixed and Varied Operating Parameters

Cycle Time	t_s (s)	100, 200, 300, 400, 500	Four Step Times Equal
	t_c (s)	400, 800, 1200, 1600, 2000	
Feed Concentration	$y_{F,CO2}$	0.15	
	$y_{F,N2}$	0.75	
	$y_{F,H2O}$	0.10	
Pressure Ratio	P_H/P_L	4, 6, 8, 10, 12	
	P_H (kPa)	137.9 (kPa)	
Purge to Feed Ratios	γ	0.50, 0.75, 1.00, 1.25, 1.50	

Underlined parameters ---> base case conditions.

SR PSA: Effect of the Purge to feed Ratio on the CO_2 Recovery and Enrichment

$P_H = 137.9$ kPa; $y_{A,F} = 0.15$, $V_f = 1$ SLPM ($\theta = 14.4$ L STP/hr/kg)



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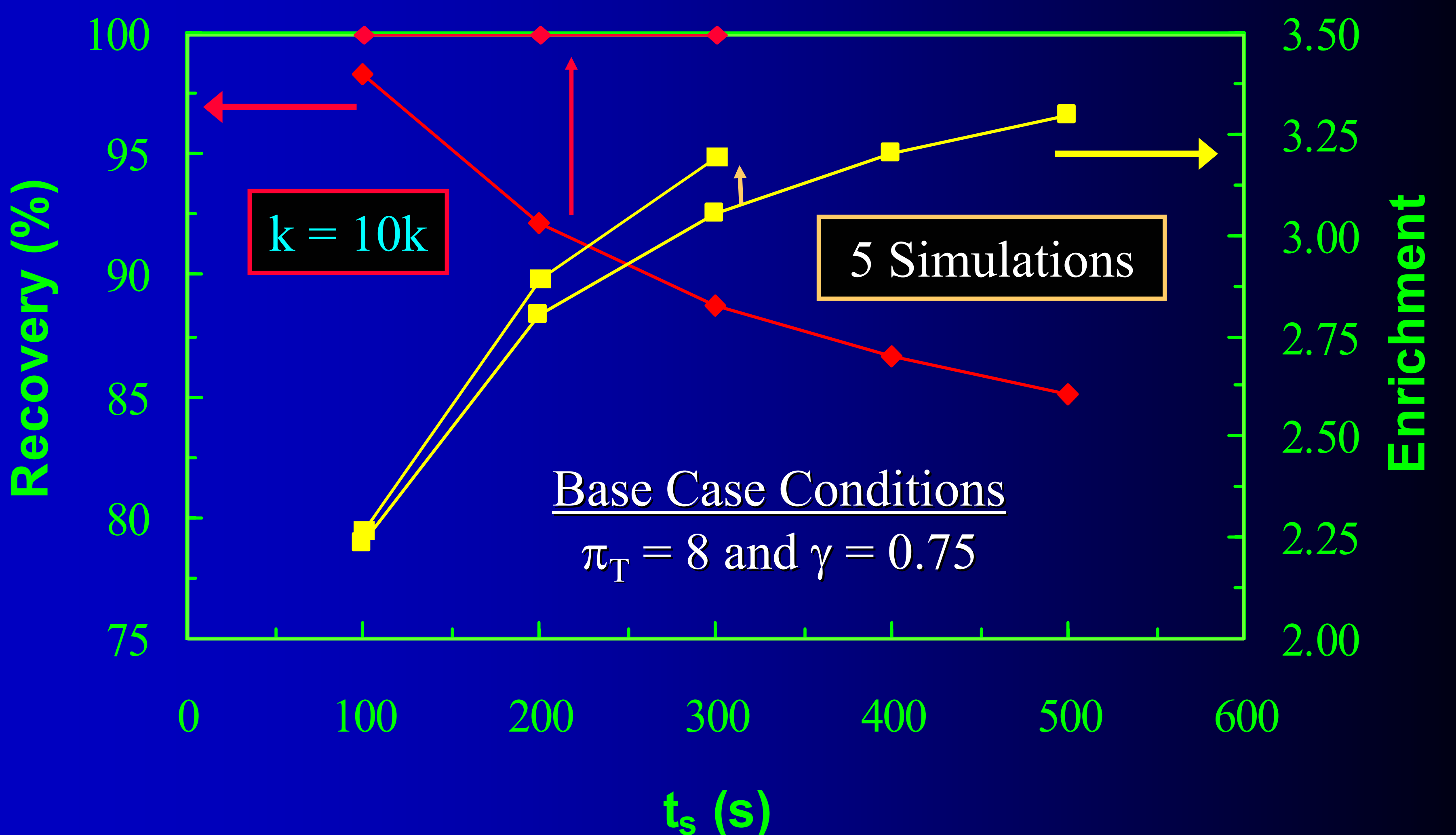

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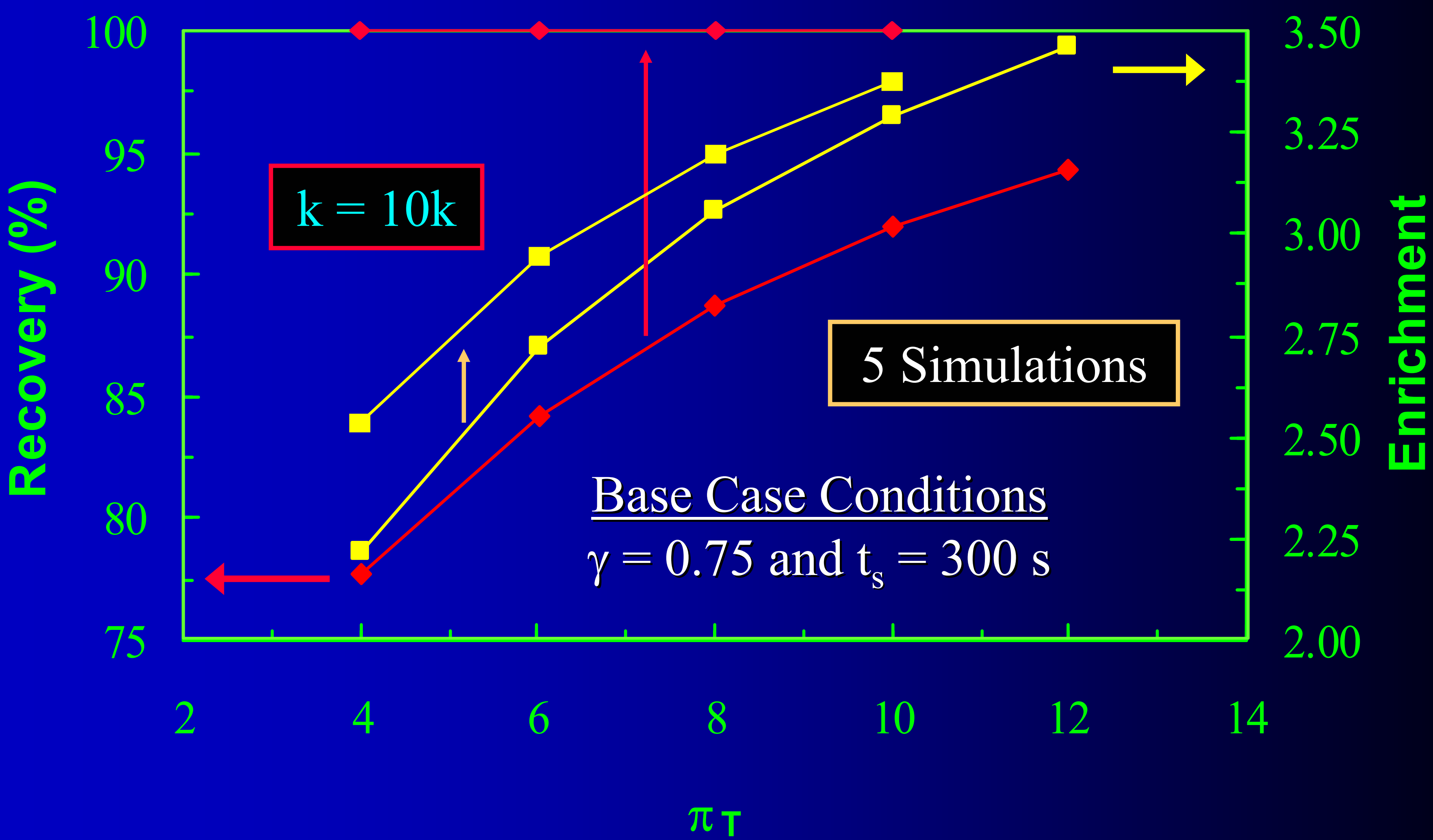
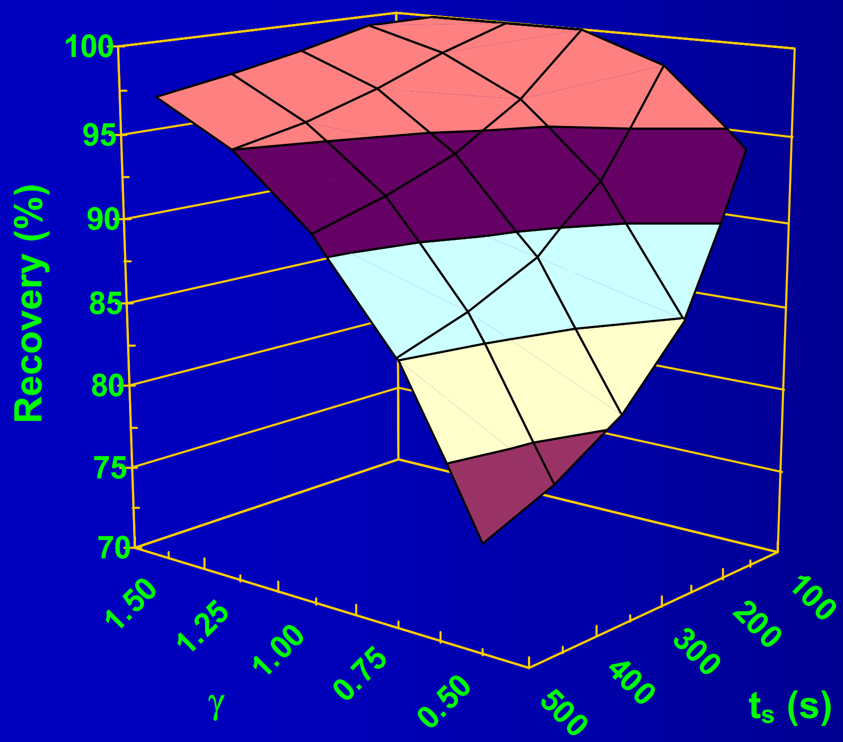
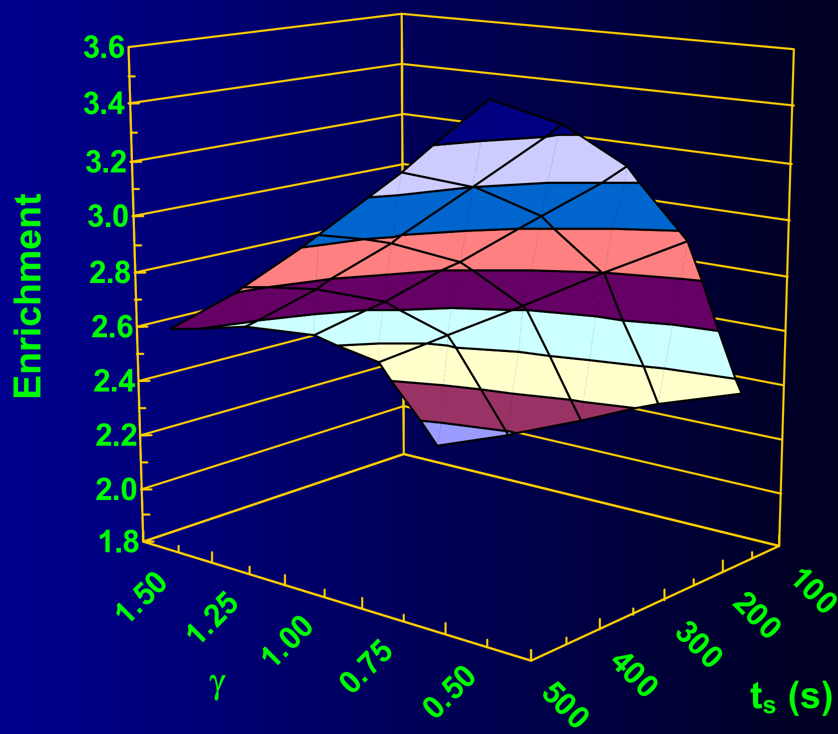


Effect of the Purge to Feed Ratio and Cycle Step Time on the CO_2 Recovery and Enrichment

$\pi_T = 8$, $P_H = 137.9$ kPa; $y_{A,F} = 0.15$, $V_f = 1$ SLPM ($\theta = 14.4$ L STP/hr/kg)

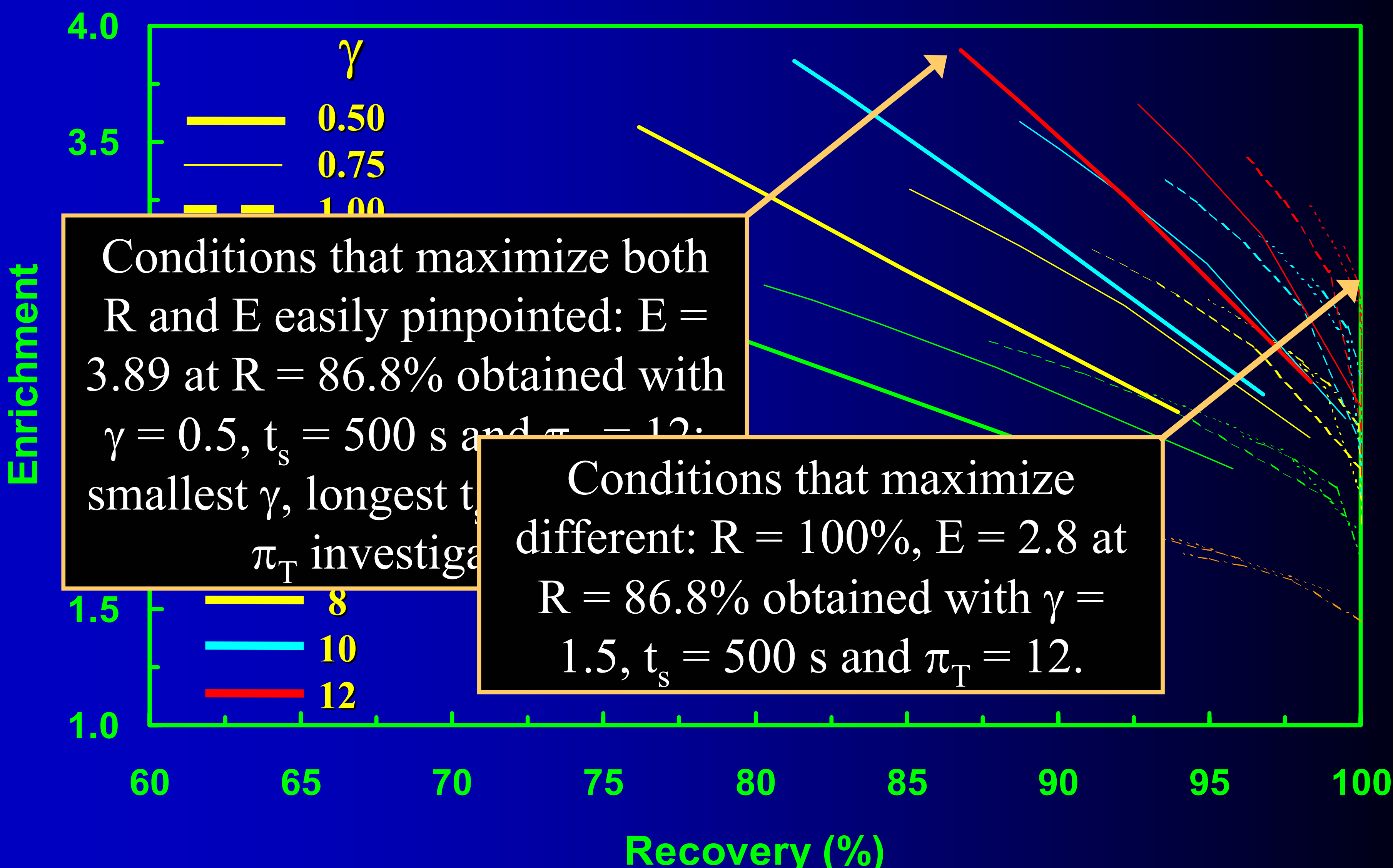




SR PSA: 25 Simulations

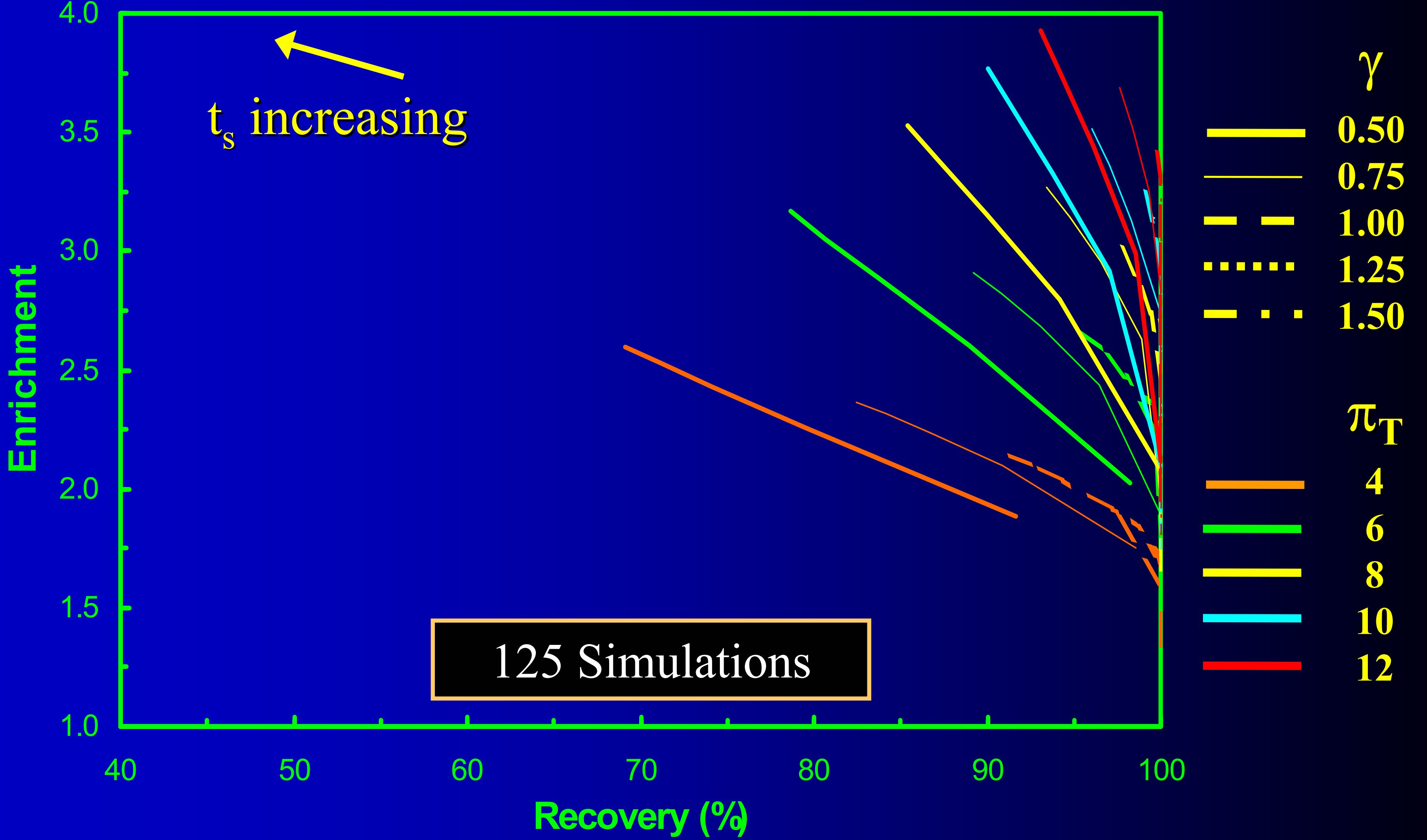
CO_2 Recovery and Enrichment Performance Curves

$P_H = 137.9$ kPa; $y_{A,F} = 0.15$, $V_f = 1$ SLPM ($\theta = 14.4$ L STP/hr/kg)



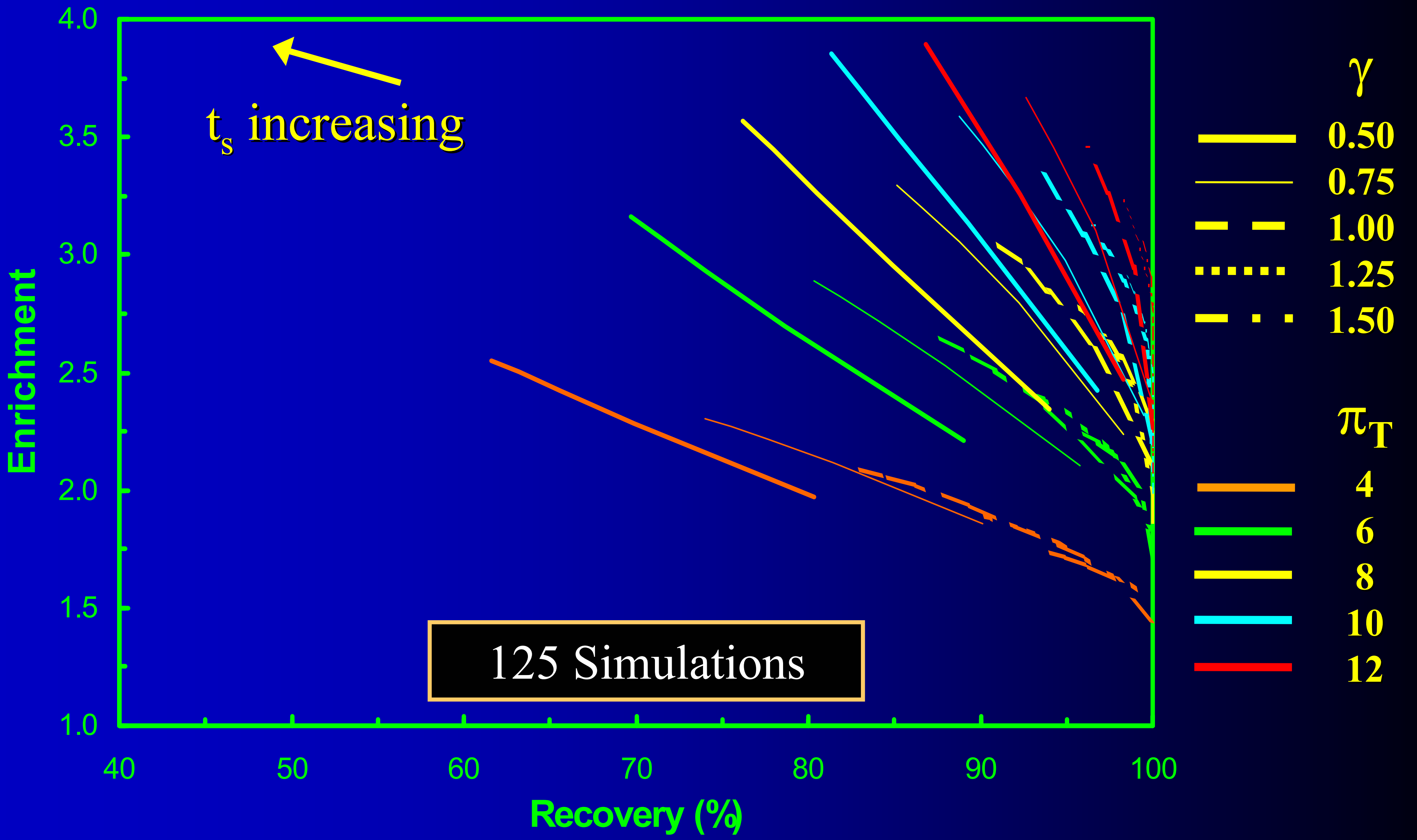
CO_2 Recovery and Enrichment Performance Curves

$P_H = 137.9$ kPa; $y_{A,F} = 0.15$, $V_f = 0.75$ SLPM ($\theta = 10.8$ L STP/hr/kg)



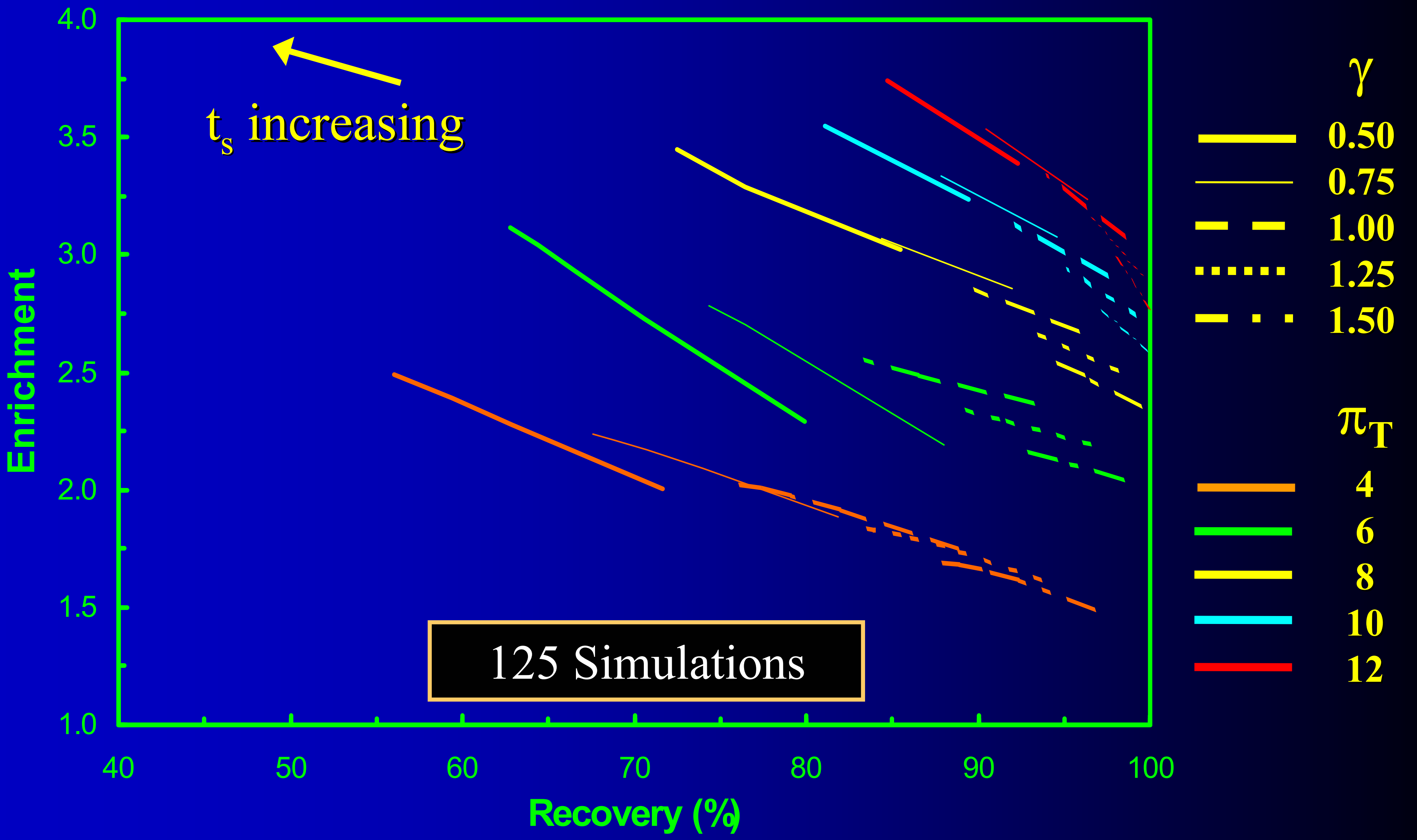
CO_2 Recovery and Enrichment Performance Curves

$P_H = 137.9$ kPa; $y_{A,F} = 0.15$, $V_f = 1.00$ SLPM ($\theta = 14.4$ L STP/hr/kg)



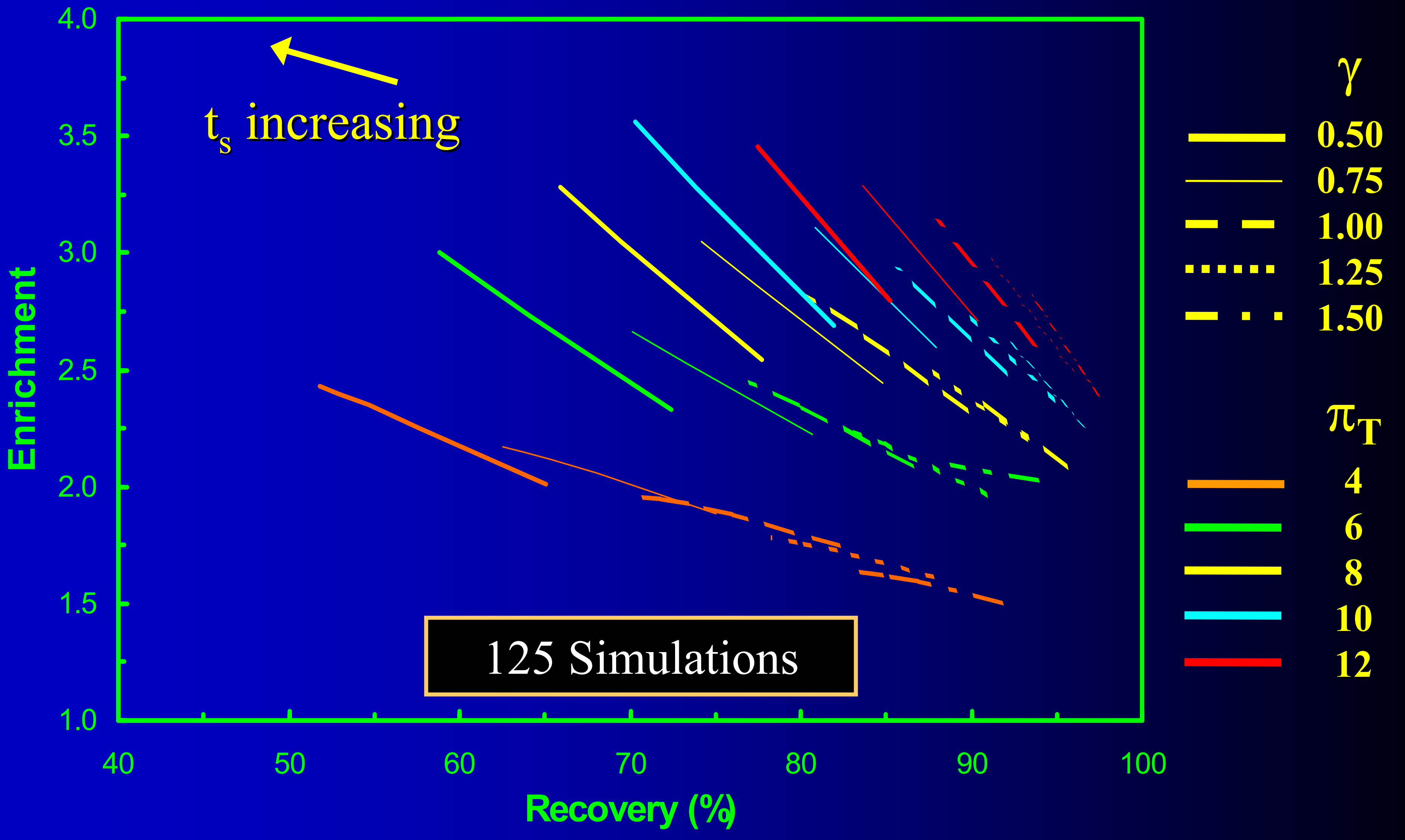
CO_2 Recovery and Enrichment Performance Curves

$P_H = 137.9$ kPa; $y_{A,F} = 0.15$, $V_f = 1.25$ SLPM ($\theta = 18.0$ L STP/hr/kg)



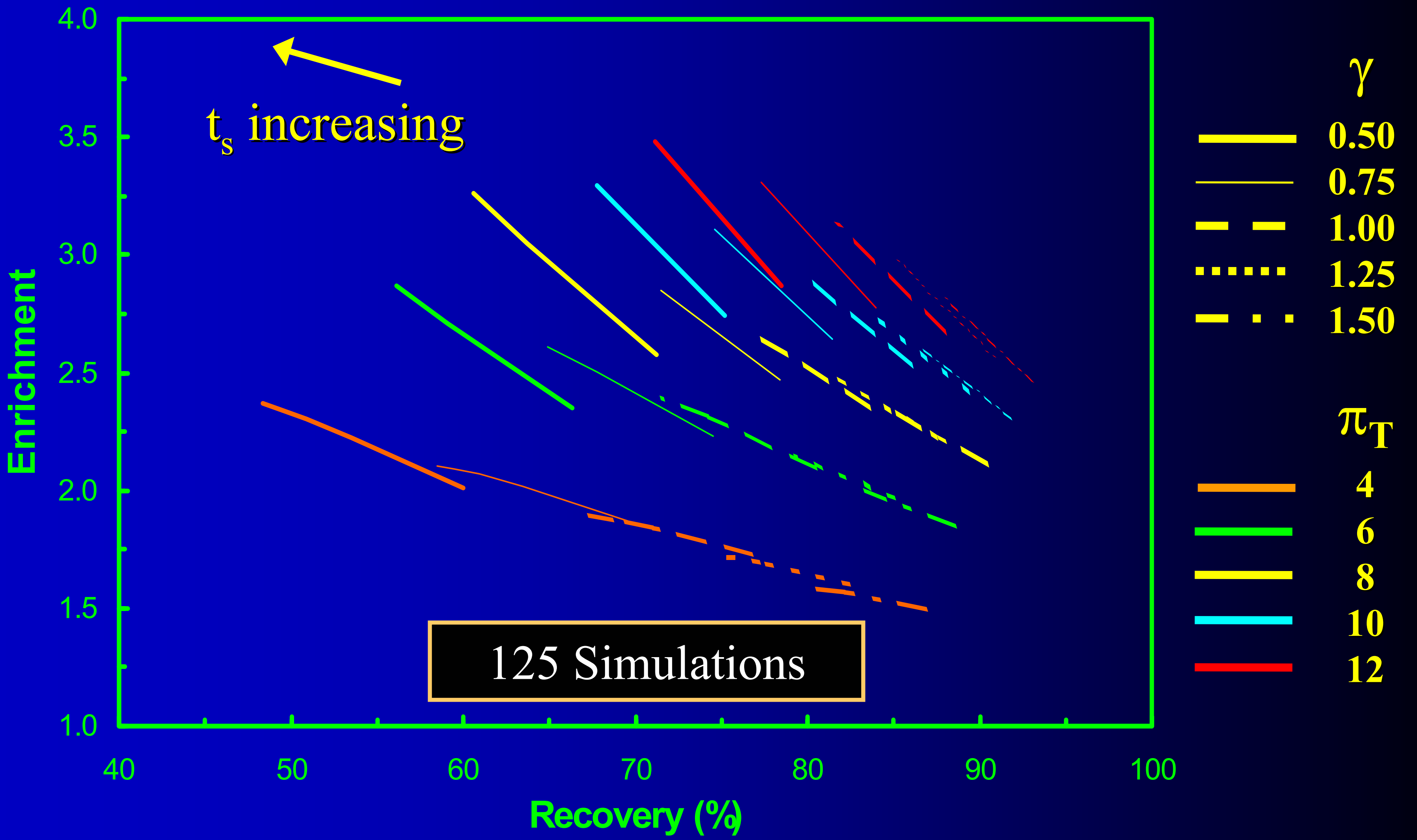
CO_2 Recovery and Enrichment Performance Curves

$P_H = 137.9$ kPa; $y_{A,F} = 0.15$, $V_f = 1.50$ SLPM ($\theta = 21.6$ L STP/hr/kg)



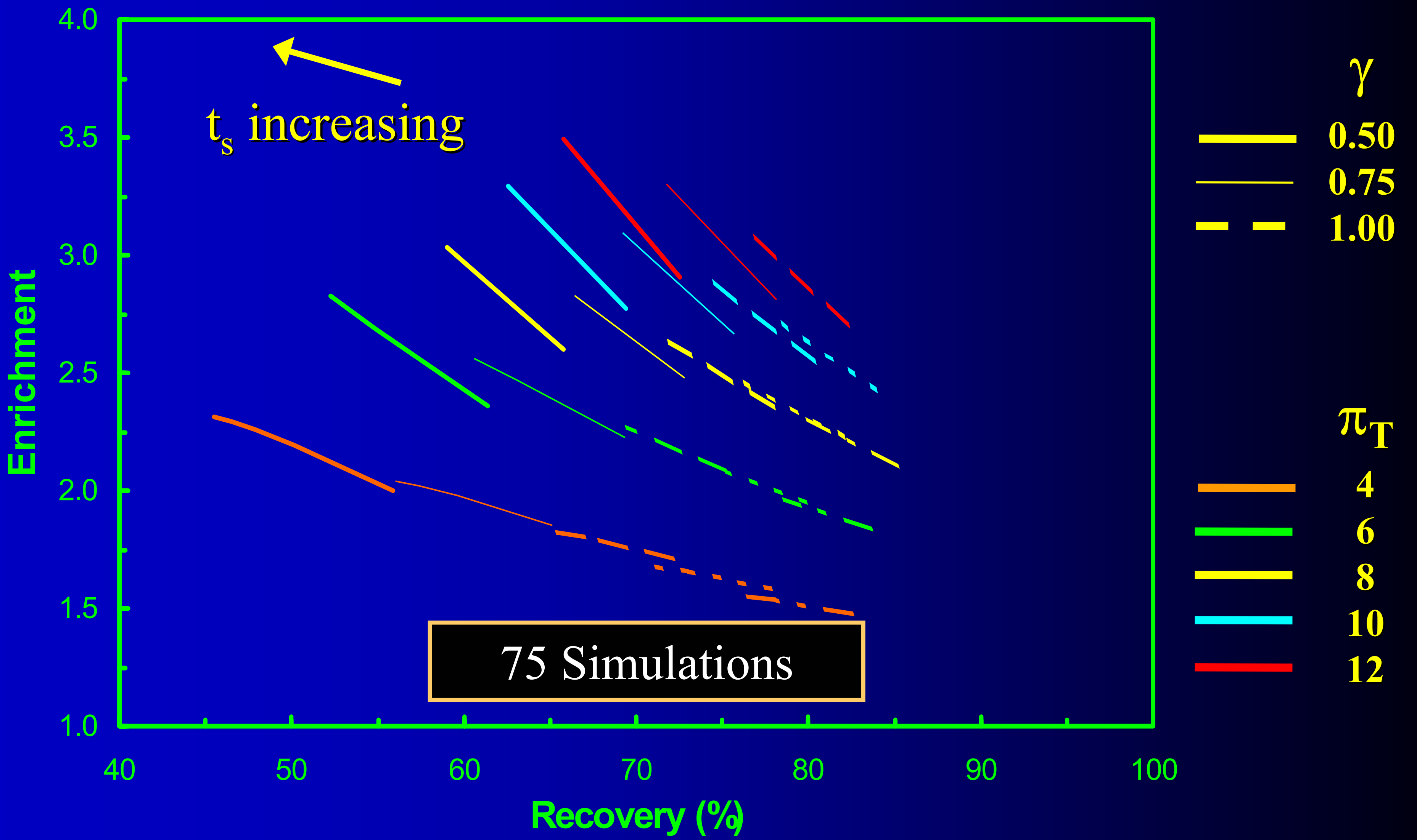
CO_2 Recovery and Enrichment Performance Curves

$P_H = 137.9$ kPa; $y_{A,F} = 0.15$, $V_f = 1.75$ SLPM ($\theta = 25.2$ L STP/hr/kg)



CO_2 Recovery and Enrichment Performance Curves

$P_H = 137.9$ kPa; $y_{A,F} = 0.15$, $V_f = 2.00$ SLPM ($\theta = 28.8$ L STP/hr/kg)



Stripping Reflux (SR) PSA Cycle with Co-Current Blowdown

- 5-step cycle, with co-current blowdown step
- co-current blowdown mainly increases CO_2 enrichment

Bed	cyc step	cyc step	cyc step	cyc step	cyc step
1	high P feed	Co-C BD	Cnt-C BD	low P purge	LP pres
2	LP pres	high P feed	Co-C BD	Cnt-C BD	low P purge
3	low P purge	LP pres	high P feed	Co-C BD	Cnt-C BD
4	Cnt-C BD	low P purge	LP pres	high P feed	Co-C BD
5	Co-C BD	Cnt-C BD	low P purge	LP pres	high P feed

LP pres: light product pressurization

high P feed: high pressure feed

Co-C BD: co-current blowdown to P_I

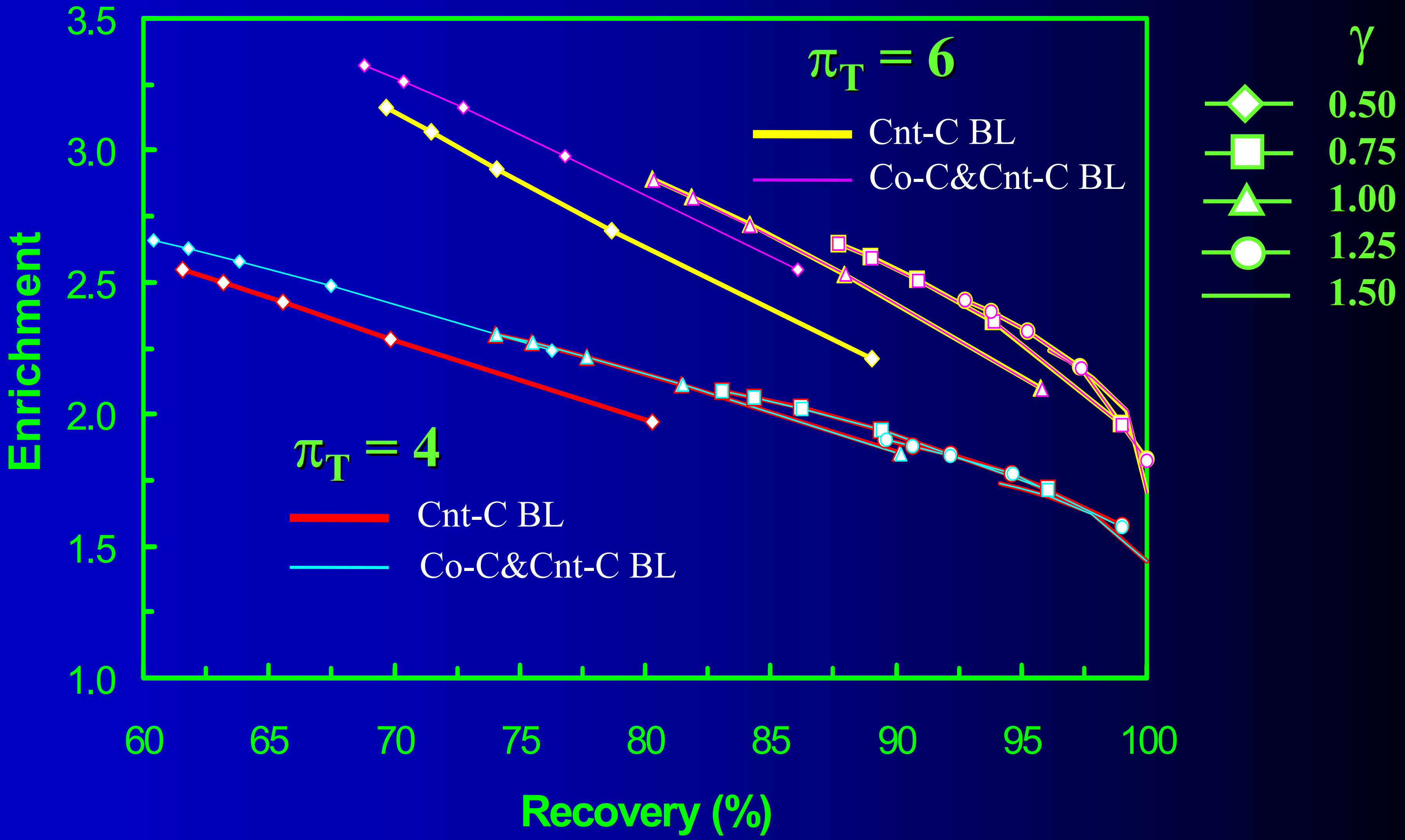
Cnt-C BD: counter-current blowdown to P_L

low P purge: low pressure purge

Co-current and counter-current blowdown step times equal, and intermediate pressure $P_I = P_{atm}$.

CO_2 Recovery and Enrichment Performance Curves

$P_H = 137.9$ kPa; $y_{A,F} = 0.15$, $V_f = 1.00$ SLPM ($\theta = 14.4$ L STP/hr/kg)



High Temperature ER PSA Cycle

- 4-step, pressure and vacuum swing cycles operated at 575 K
- based on use of K-promoted HTlc adsorbent selective only for CO_2 and water insensitive
- typical stack gas or flue gas effluent treated
  - obviates need to cool, dry or pressurize the feed stream (only for VSA cycle)
  - potential to produce an enriched stream of CO_2 at high recovery

Results obtained from non-linear, isothermal equilibrium theory (NL-IET), and non-isothermal mass transfer limited (NI-MTL) modeling studies.

Enriching Reflux (ER) PSA Cycle

- 4-step ER PSA cycle
- cocurrent blowdown and heavy product pressurization
- many other cycle sequences possible with ER PSA
- high purity heavy product produced

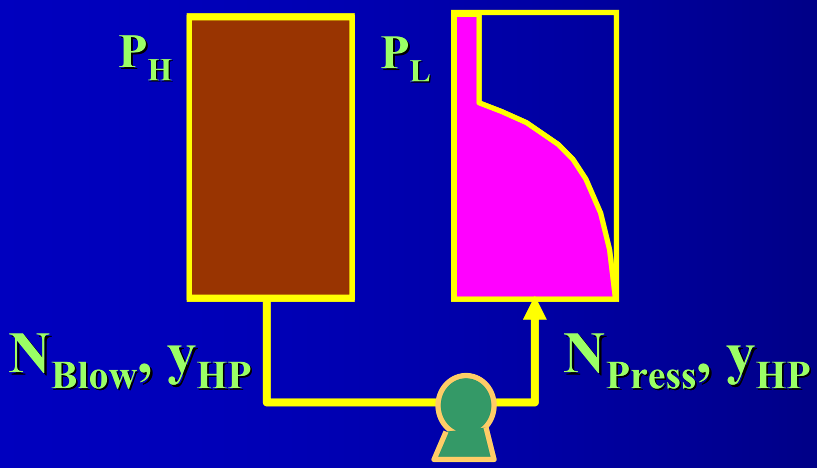
Bed	cyc step	cyc step	cyc step	cyc step
1	low P feed	HP pres	high P purge	Co-C BD
2	Co-C BD	low P feed	HP pres	high P purge
3	low P purge	Co-C BD	low P feed	HP pres
4	HP pres	high P purge	Co-C BD	low P feed

HP pres: heavy product pressurization
low P feed: low pressure feed
C0-C BD: cocurrent blowdown
high P purge: high pressure purge

Four beds needed for continuous feed and products cycle; two independent ER PSA units.

Enriching PSA Cycle

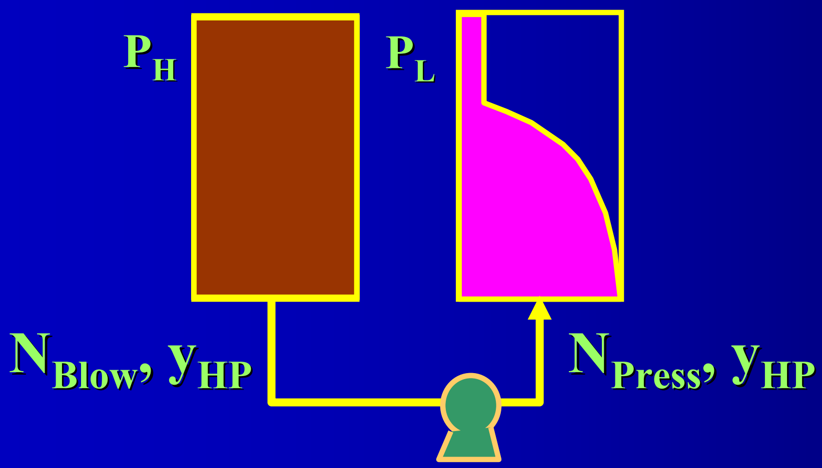
Pressurization and Blowdown Steps



$$\boxed{y_{HP} = 1.0}$$

Enriching PSA Cycle

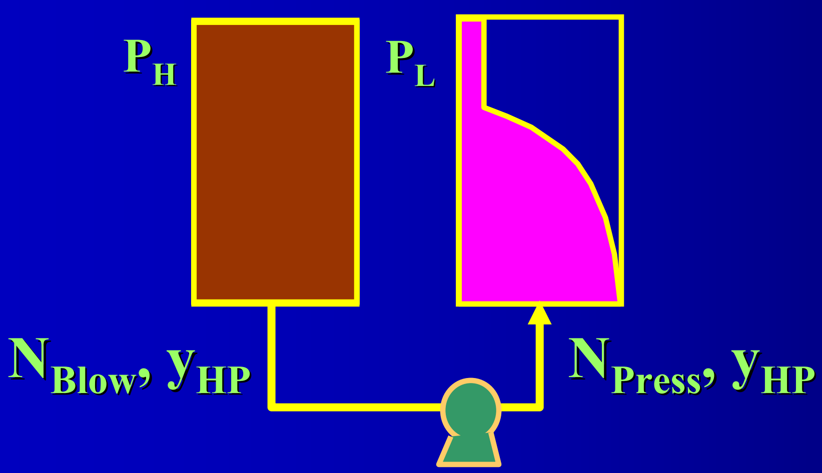
Pressurization and Blowdown Steps Begin

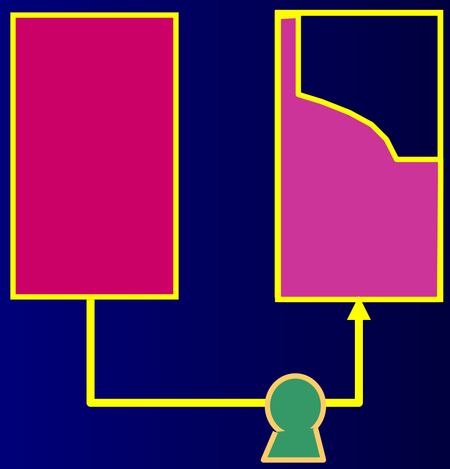


$$y_{HP} = 1.0$$

Enriching PSA Cycle

Pressurizing and Blowing Down

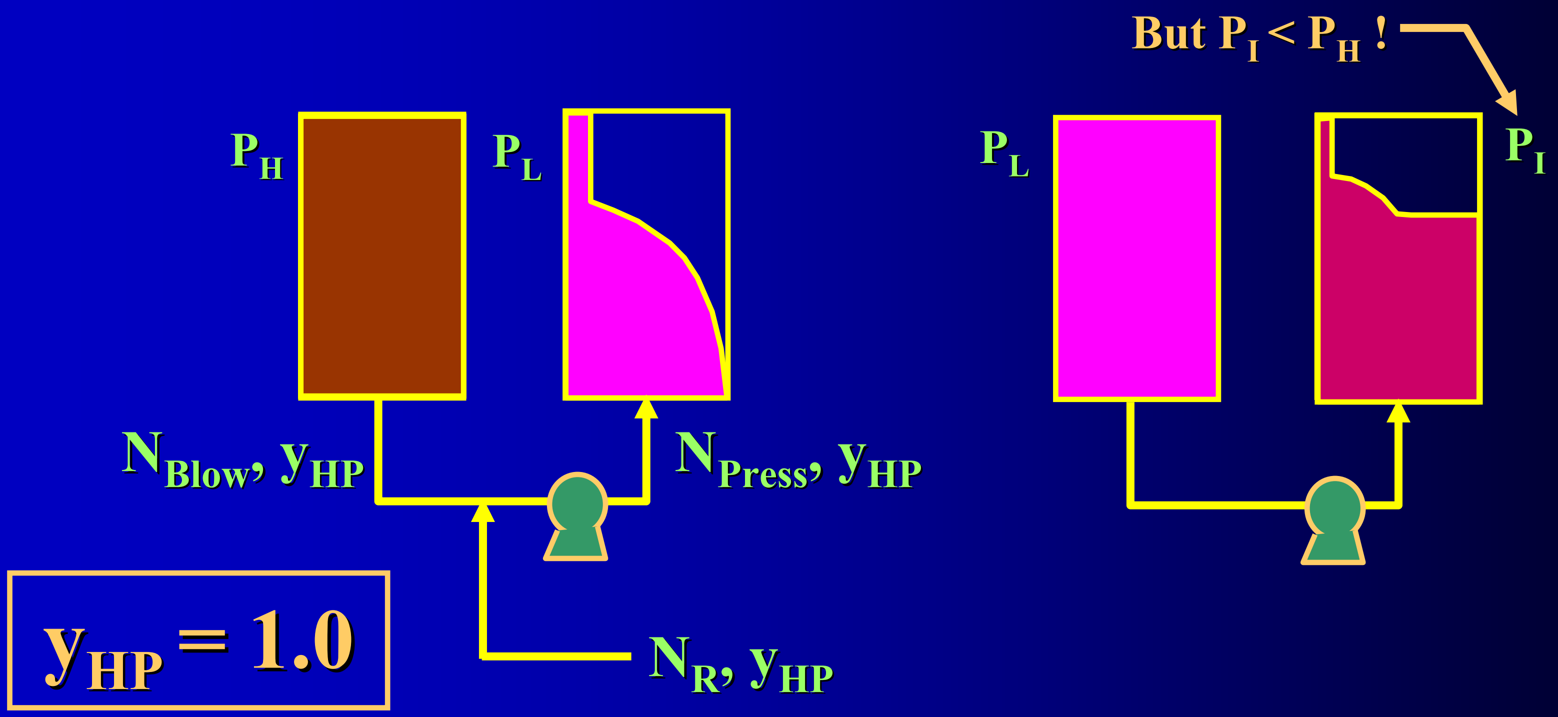




$\boxed{y_{HP} = 1.0}$

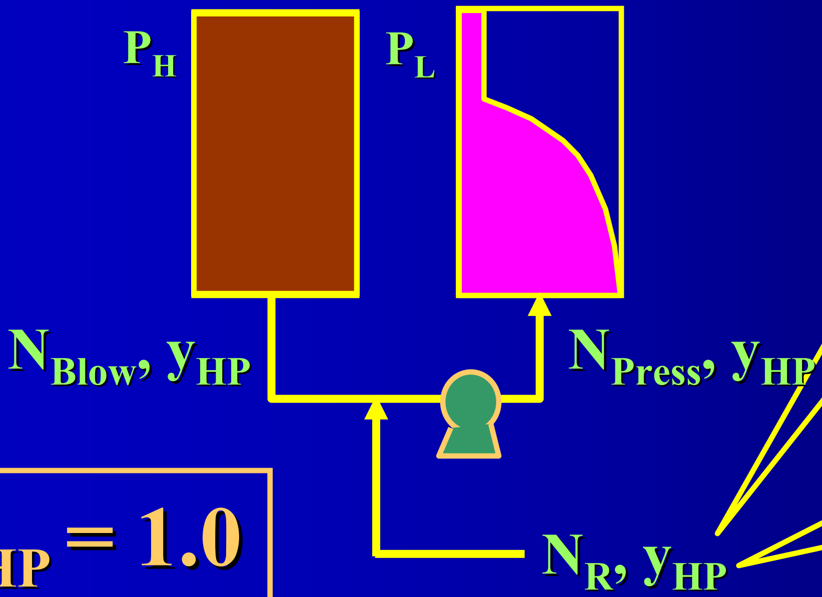
Enriching PSA Cycle

Pressurizing and Blowing Down



Enriching PSA Cycle

Pressurization and Blowdown Steps



$y_{HP} = 1.0$

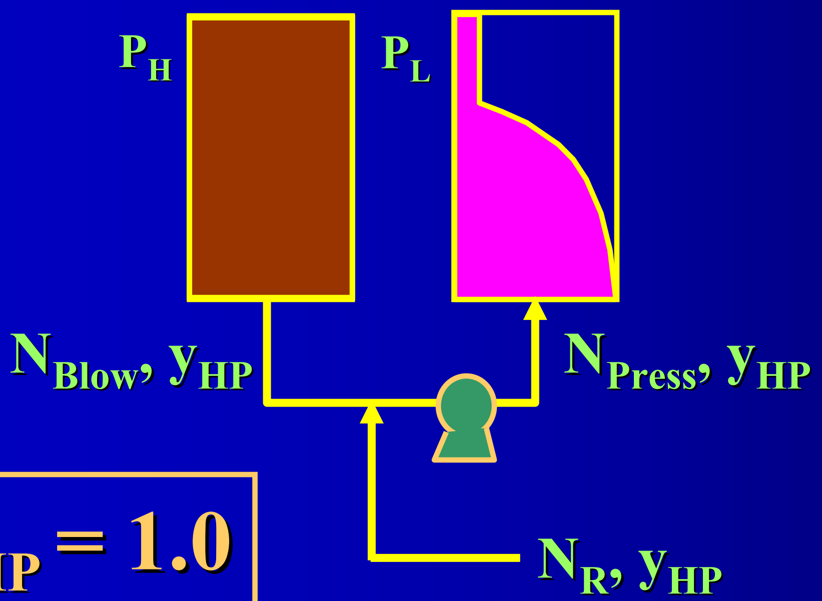
Additional pressurization gas needed for non-linear systems.

Unlike linear systems $N_{press} \neq N_{blow}$; in fact, at conditions studied here, $N_{press} > N_{blow}$.

This flow is obtained from the feed step.

Enriching PSA Cycle

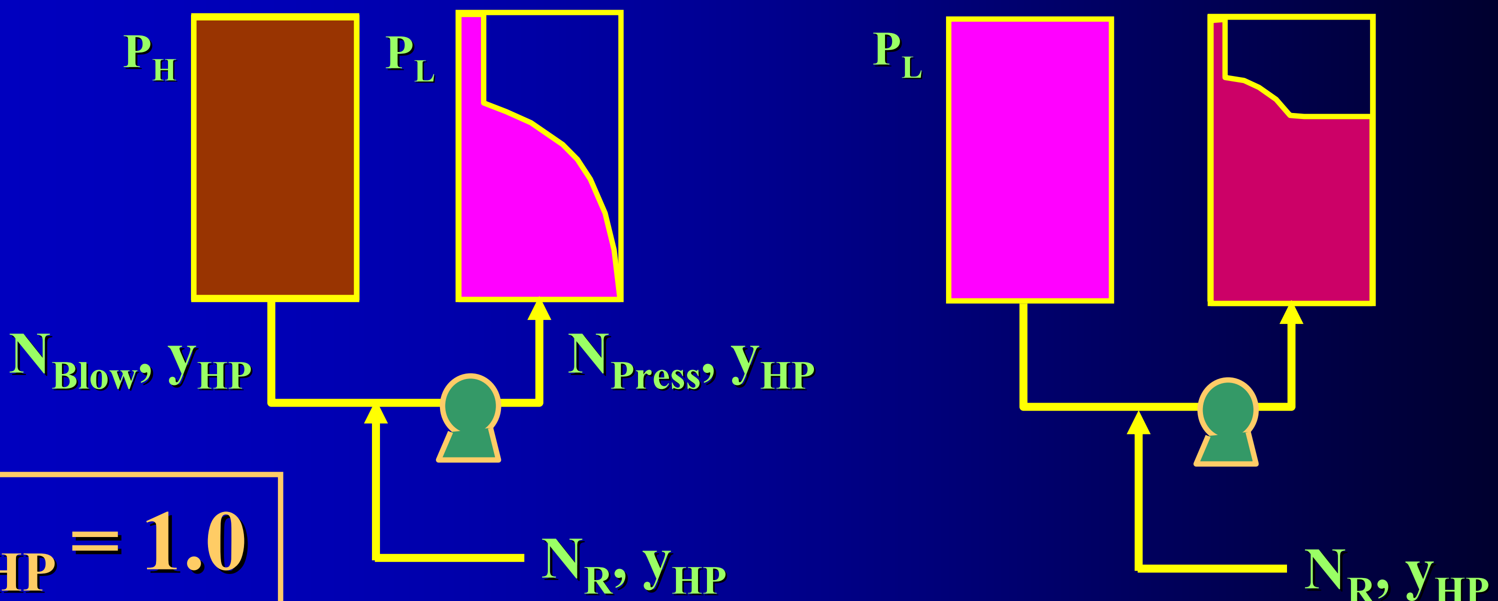
Pressurizing and Blowing Down



$y_{HP} = 1.0$

Enriching PSA Cycle

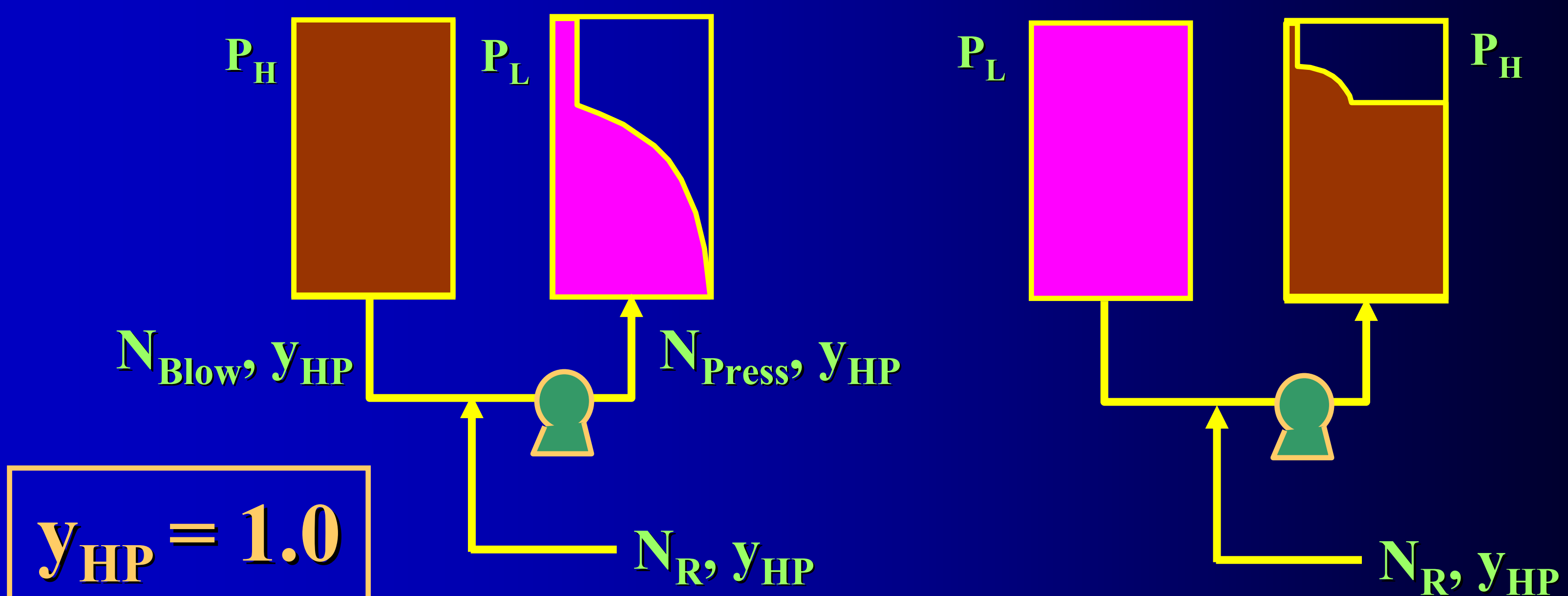
Pressurizing and Blowing Down



$$\boxed{y_{HP} = 1.0}$$

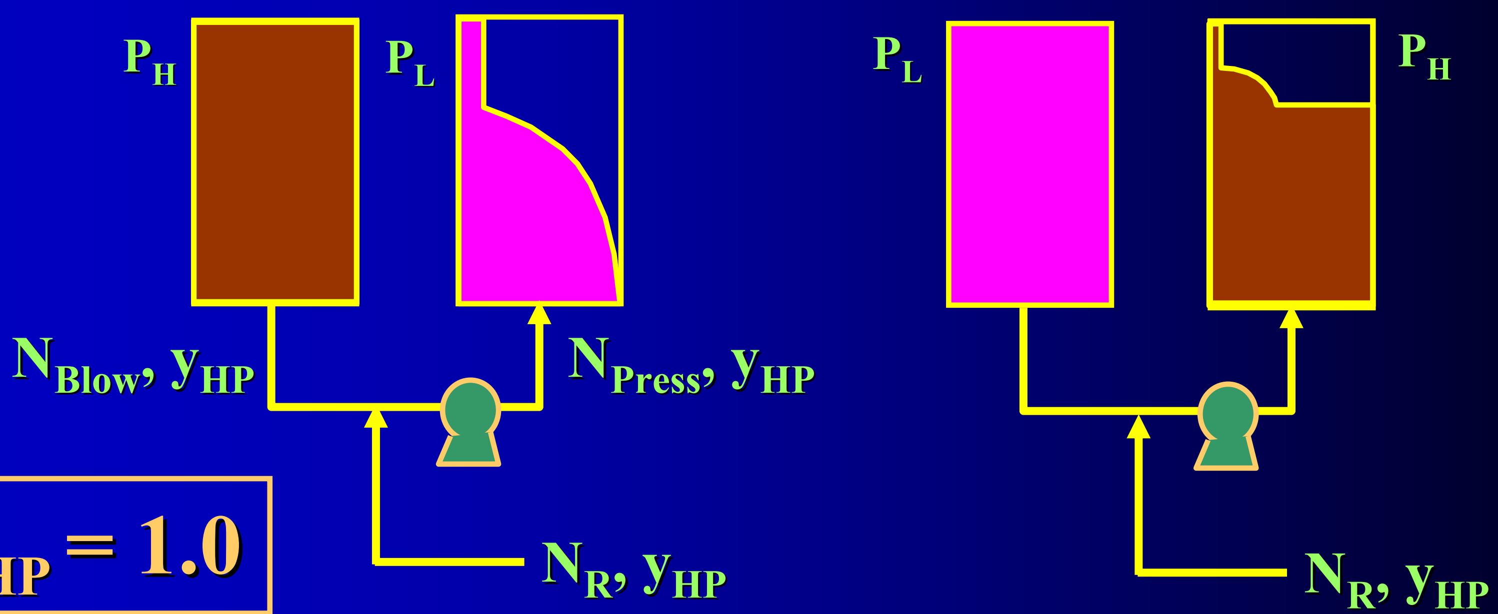
Enriching PSA Cycle

Pressurizing and Blowing Down



Enriching PSA Cycle

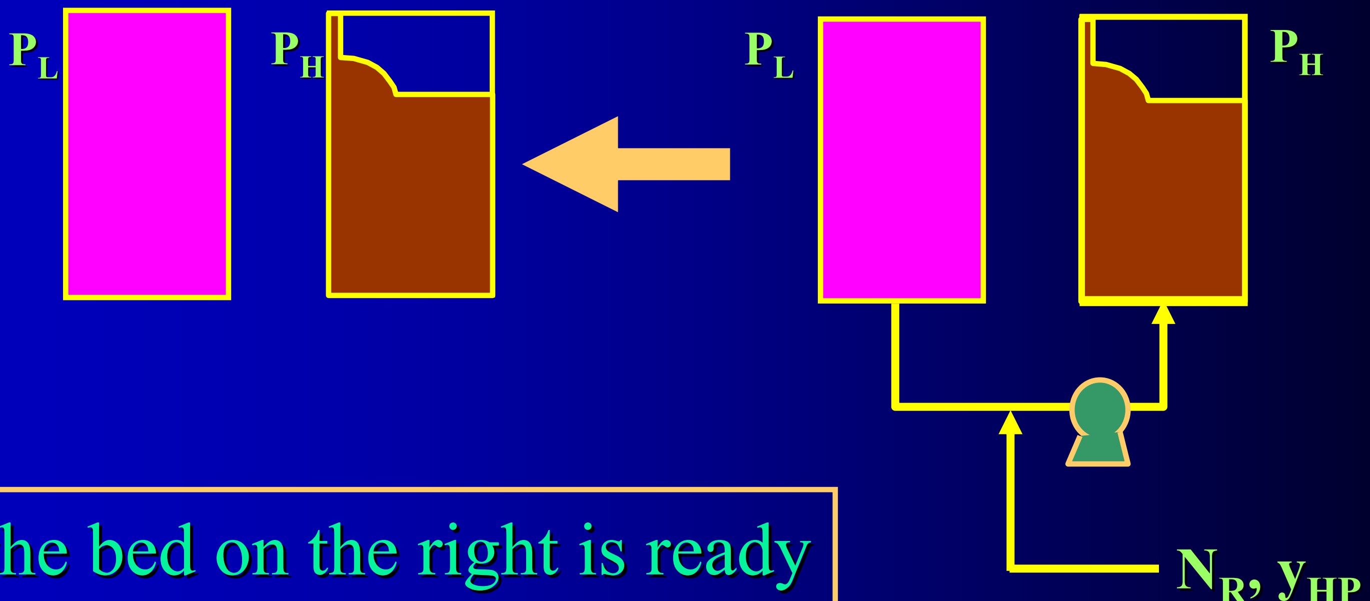
Pressurization and Blowdown Steps End



$\boxed{y_{HP} = 1.0}$

Enriching PSA Cycle

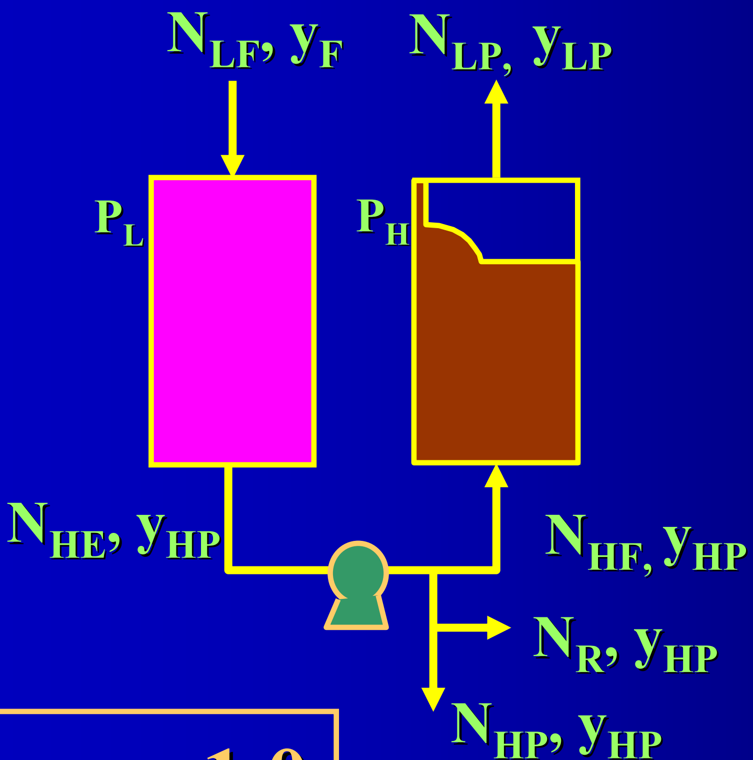
Pressurization and Blowdown Steps End



Now, the bed on the right is ready to be fed at $P_{L.}$

Enriching PSA Cycle

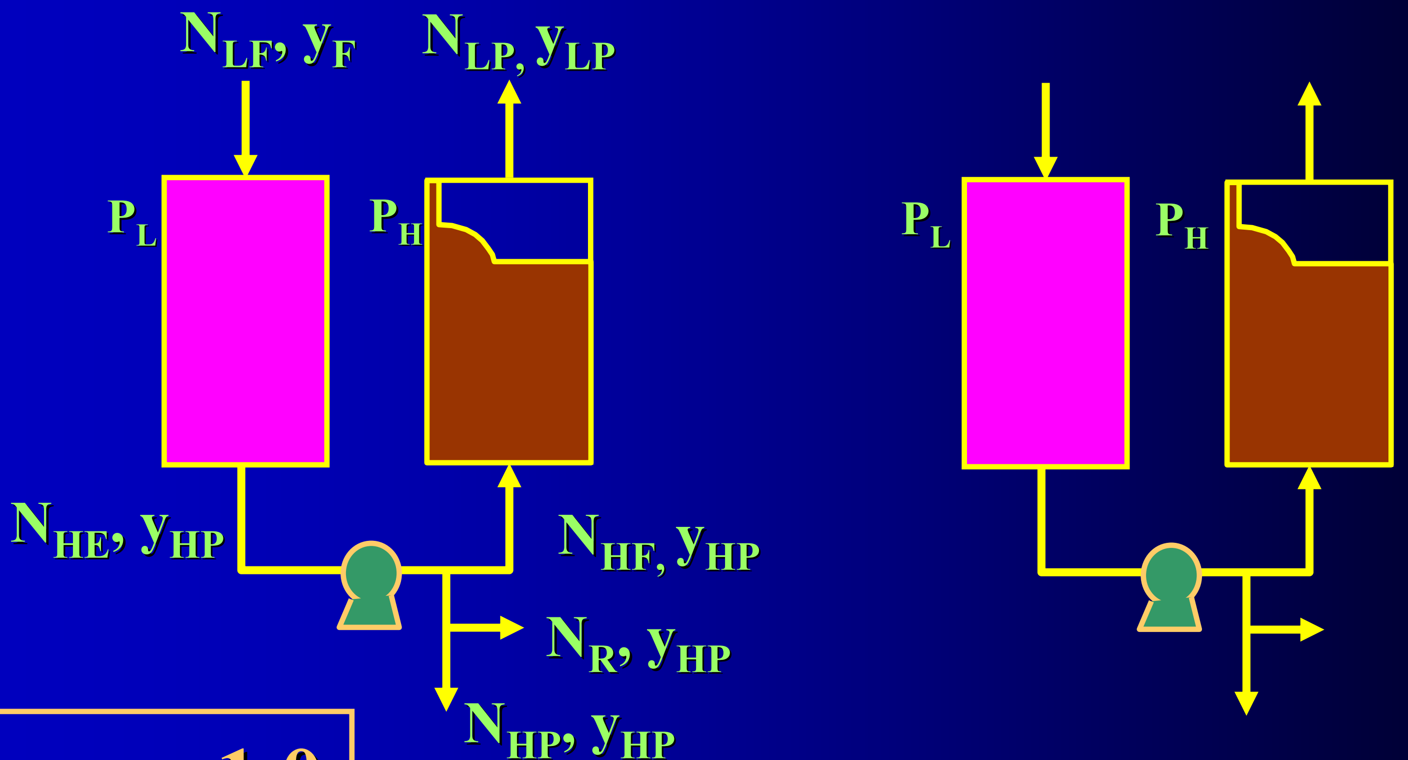
Feed and Purge Steps



$$\boxed{y_{HP} = 1.0}$$

Enriching PSA Cycle

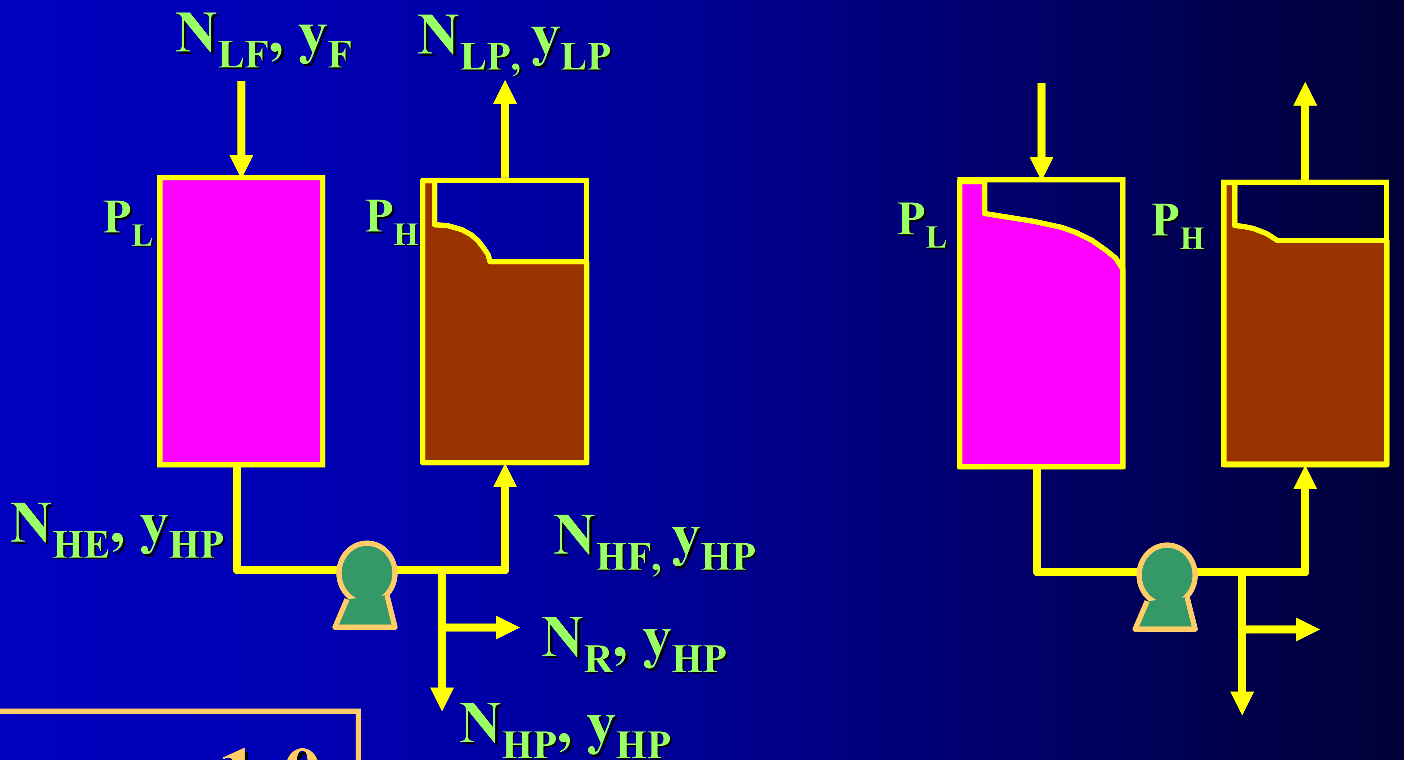
Feed and Purge Steps Begin



$$y_{HP} = 1.0$$

Enriching PSA Cycle

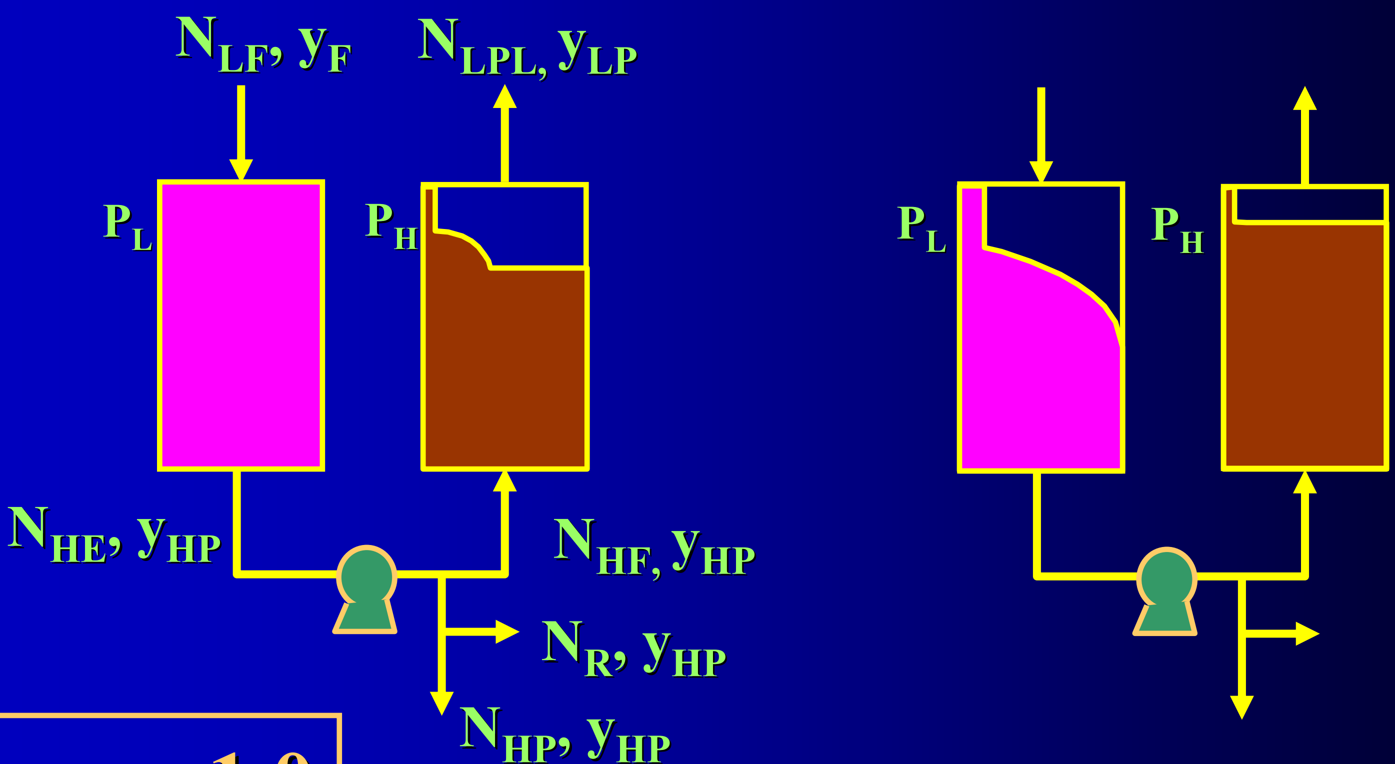
Feeding and Purging



$$\boxed{y_{HP} = 1.0}$$

Enriching PSA Cycle

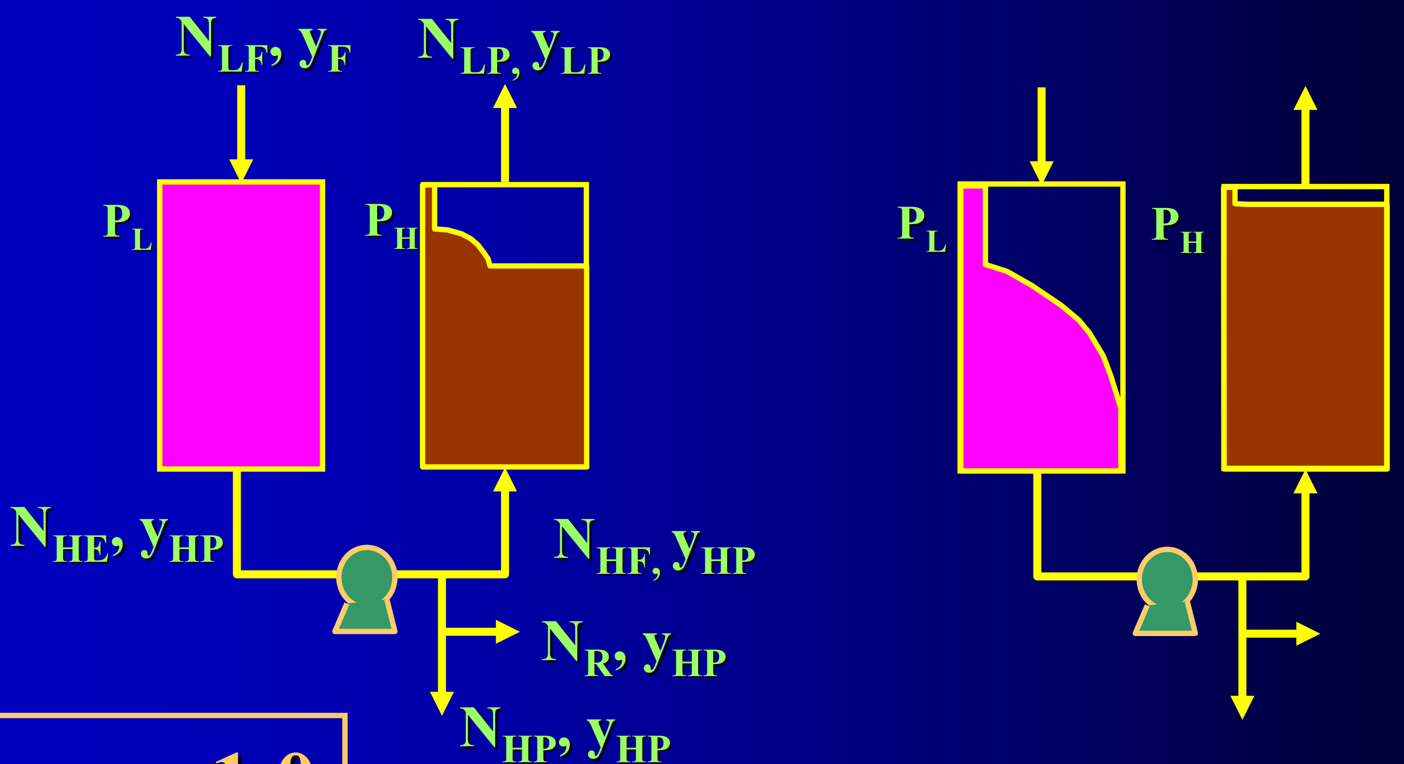
Feeding and Purging



$$\boxed{y_{HP} = 1.0}$$

Enriching PSA Cycle

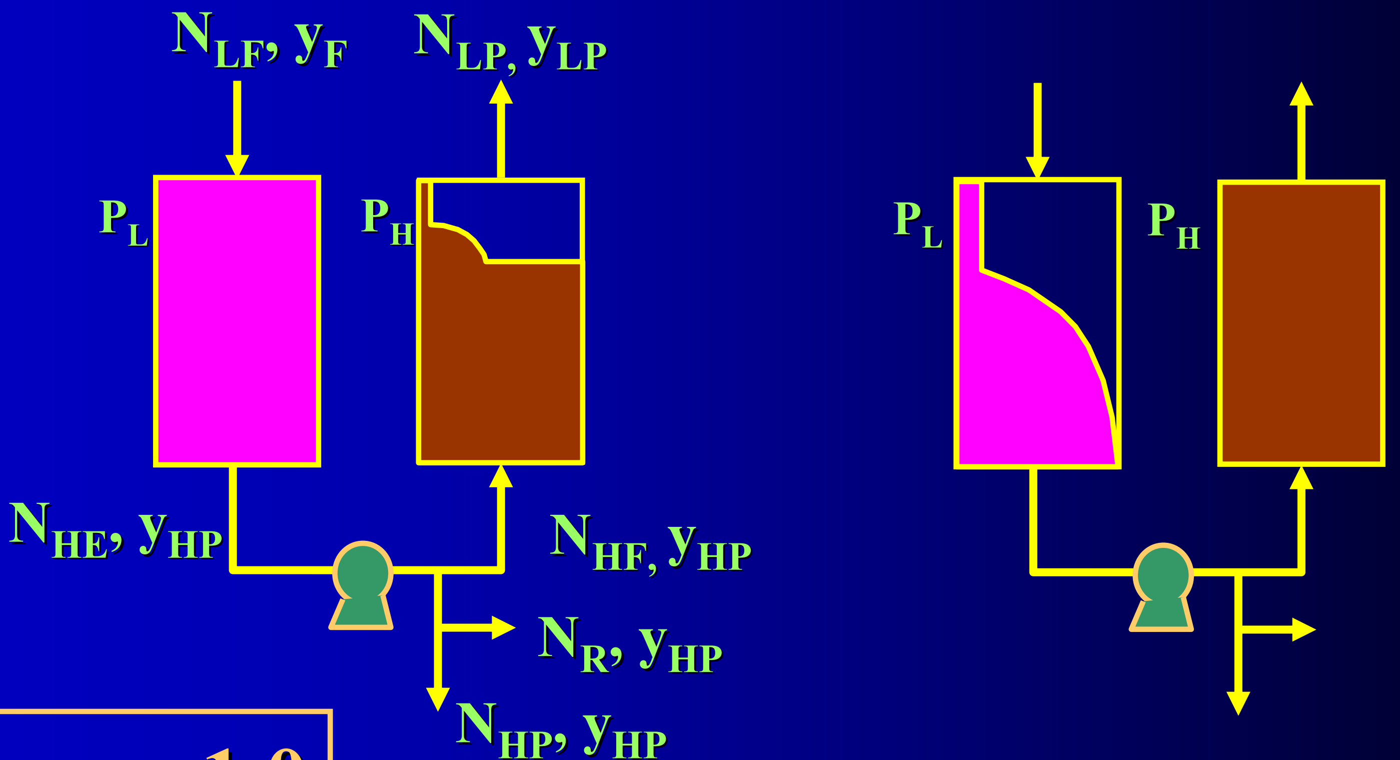
Feeding and Purging



$y_{HP} = 1.0$

Enriching PSA Cycle

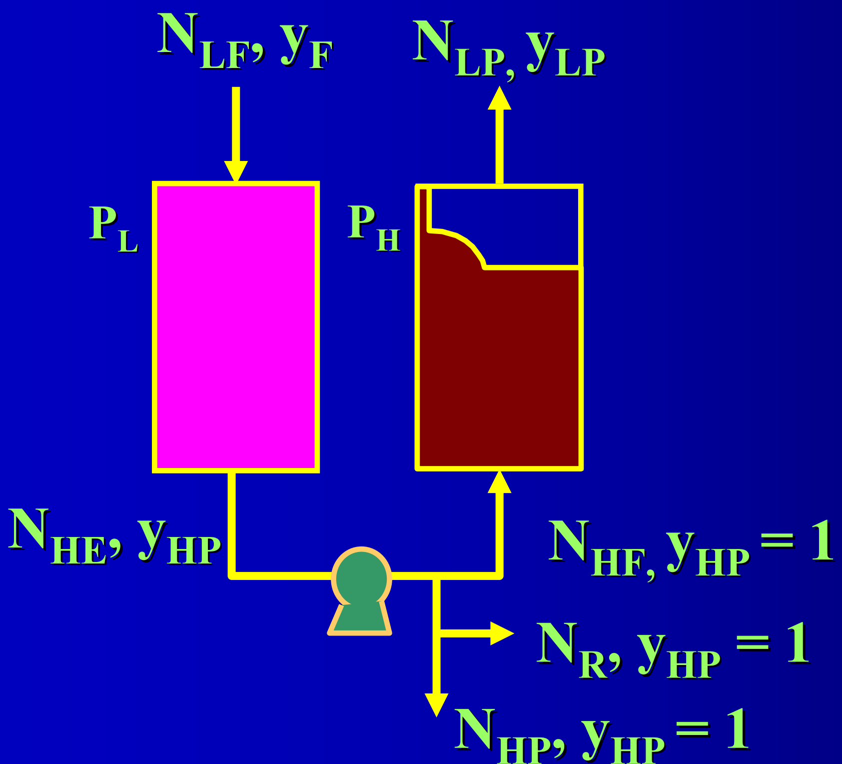
Feed and Purge Steps End



$$\boxed{y_{HP} = 1.0}$$

Definition of Parameters

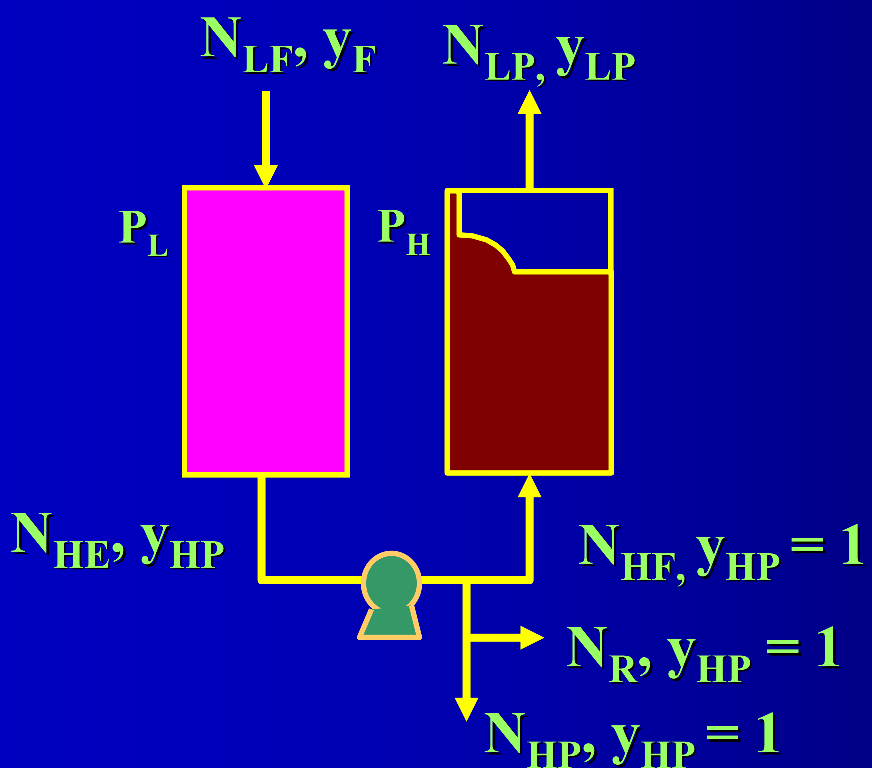
Degree of Depletion



$$D_d = \frac{y_{LP}}{y_F}$$

Definition of Parameters

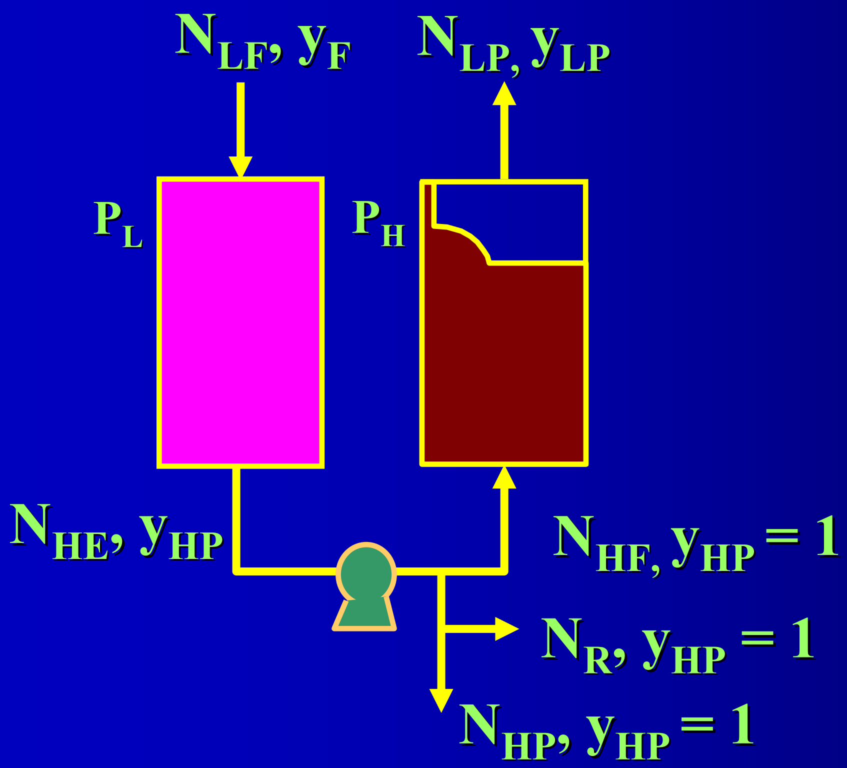
Extent of Recovery



$$E_R = \frac{N_{HP}}{y_F \cdot N_{LF}}$$

Definition of Parameters

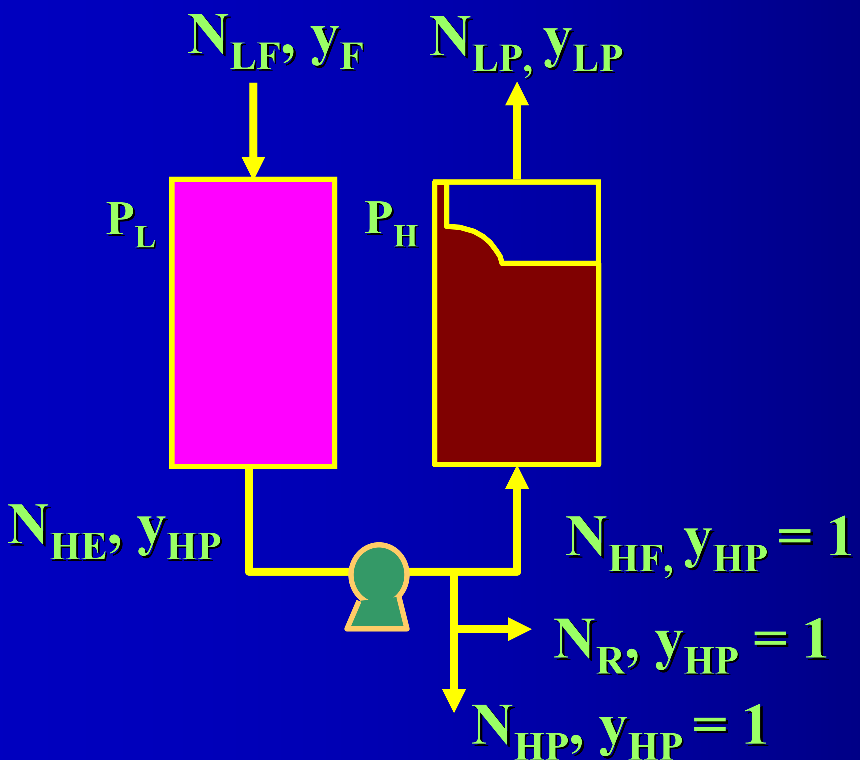
Recycle Ratio



$$R_r = \frac{N_{HF}}{N_{HE}}$$

Definition of Parameters

Pressurization Recycle



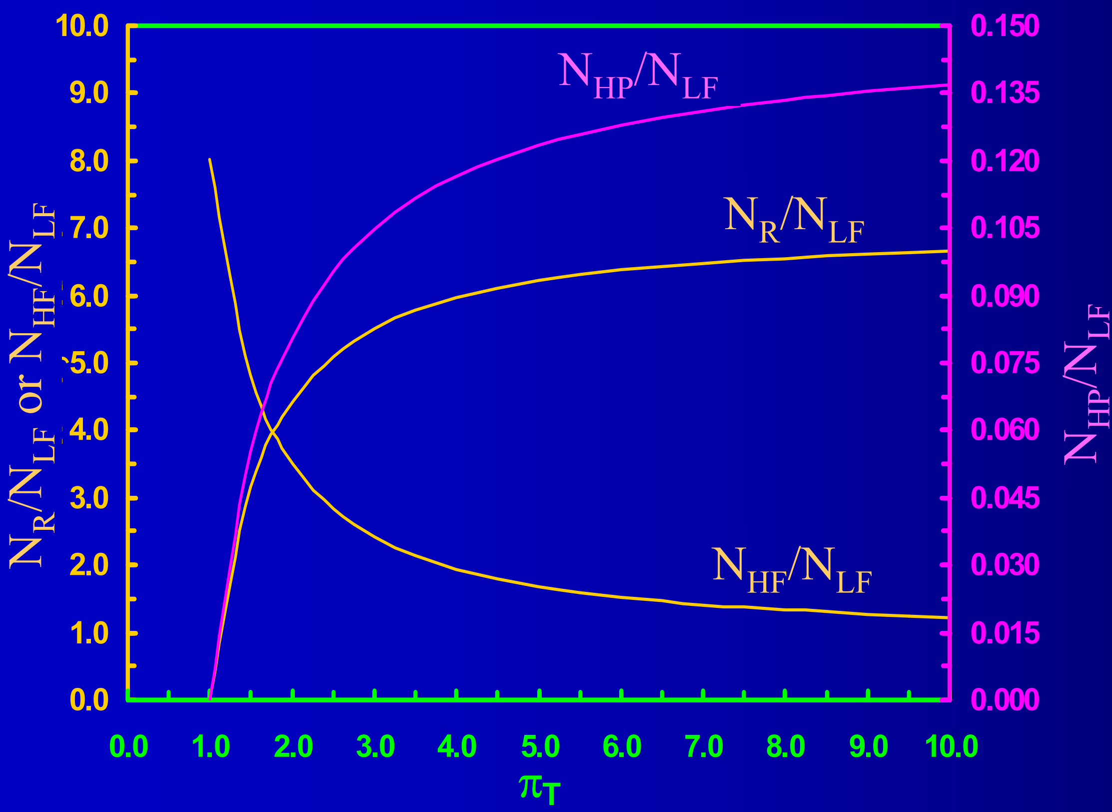
$$R_p = \frac{N_R}{N_{HE}}$$

Results of the NLIET-ER PSA Model

Effect of Pressure Ratio on N_{HE}

Conditions:

$y_F = 0.15$, $P_L = 1$ atm, $T = 575$ K



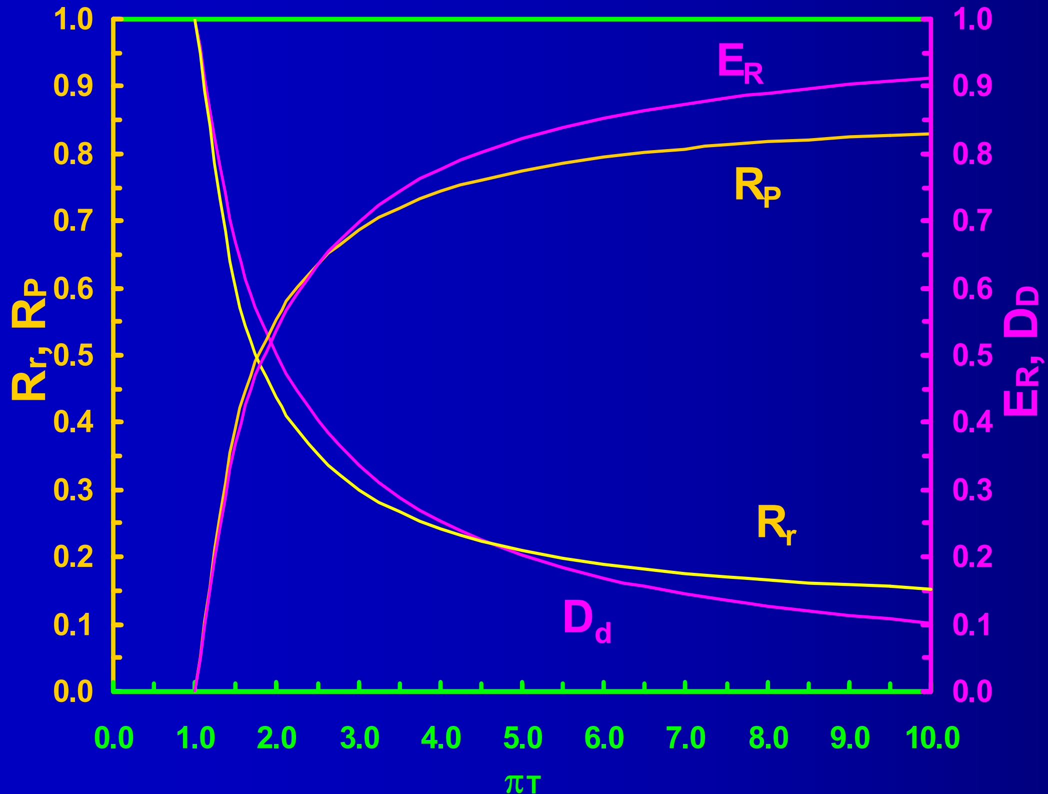
- **Performance of ER PSA process improves with pressure ratio (larger N_{HP} with π_T)**
- **As π_T increases N_{HP}/N_{LF} approaches but never larger than y_F**
- **Remarkably large values of N_{HF} and N_R (both adding up to ~ 8) due to considerable desorption and expansion of gas during feed**

Results of the NLIET-ER PSA Model

Effect of Pressure Ratio on E_R, D_d, R_p and R_r

Conditions:

$y_{A,F} = 0.15$, $P_L = 1$ atm, $T = 575$ K



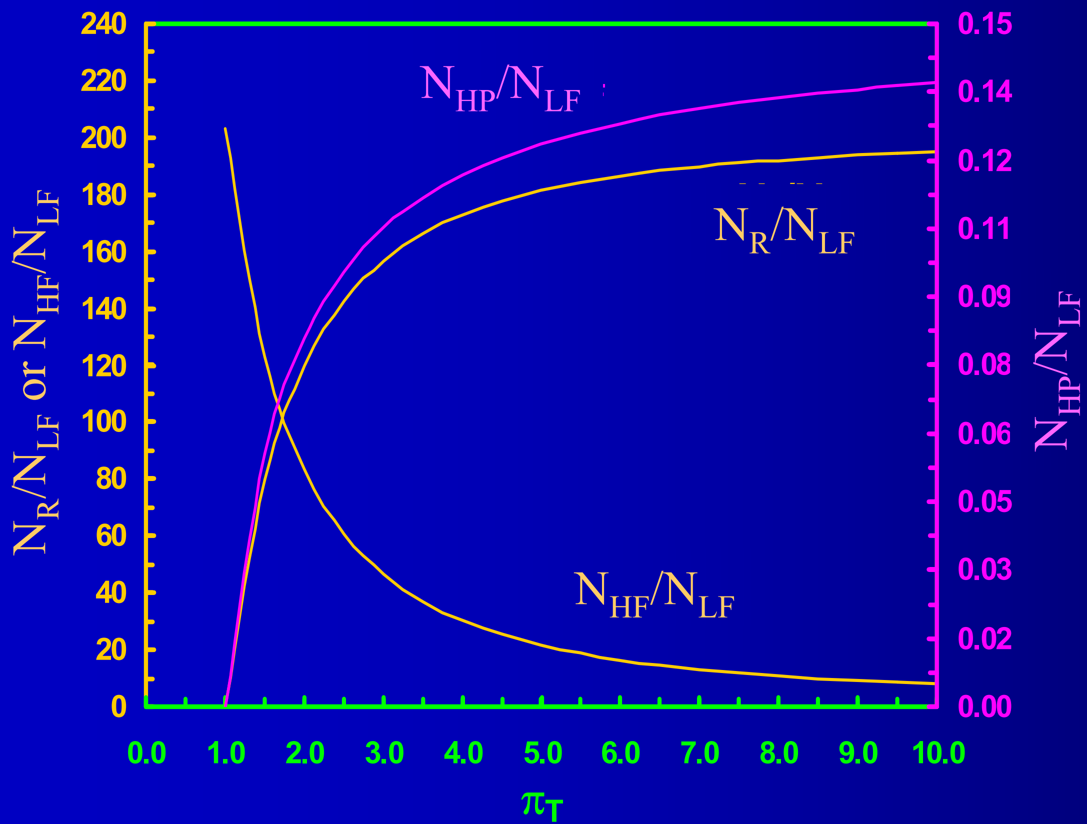
- At π_T larger than about 5.0, E_R becomes larger than 80%
- The direct consequence of this is the ever smaller concentrations of CO_2 in N_{LP}, i.e., D_d decreases
- The recycle ratio (R_r) also decreases with increasing π_T, but at the expense of increasing the pressurization recycle (R_p)

Results of the NLIET-ER PSA Model

Effect of Pressure Ratio on N_{HE} (Smaller P_L)

Conditions:

$y_{A,F} = 0.15$, $P_L = 0.1$ atm, $T = 575$ K



- Performance of ER PSA (in terms of N_{HP}/N_{LF}) does not vary significantly with smaller feed pressures (i.e., P_L)
- However, the huge flow rates at these conditions ($N_{HF} + N_R \sim 200\ N_{LF}$) could be very detrimental in terms of pump costs
- Such large flows are a direct consequence of the very large selectivities of the adsorbent for CO_2

NI-MTL ER PSA Model Assumptions

ASSUMPTIONS:

- ideal gas law
- plug-flow (negligible radial gradients)
- negligible pressure drop
- finite heat and mass transfer resistances
- mass transfer governed by linear driving force approximation
- heat transfer governed by overall heat transfer coefficient
- loading dependent heat of adsorption
- gas and adsorbed phase heat capacities equal and temperature dependent
- constant adsorbent heat capacity

SOLUTION PROCEDURE:

- **unlike ET, optimum conditions can only be found through parametric studies**
- **FORTRAN based numerical code (method of lines) used (DDASPK)**

Rigorous Model!

ER PSA: Effect of Bed Length

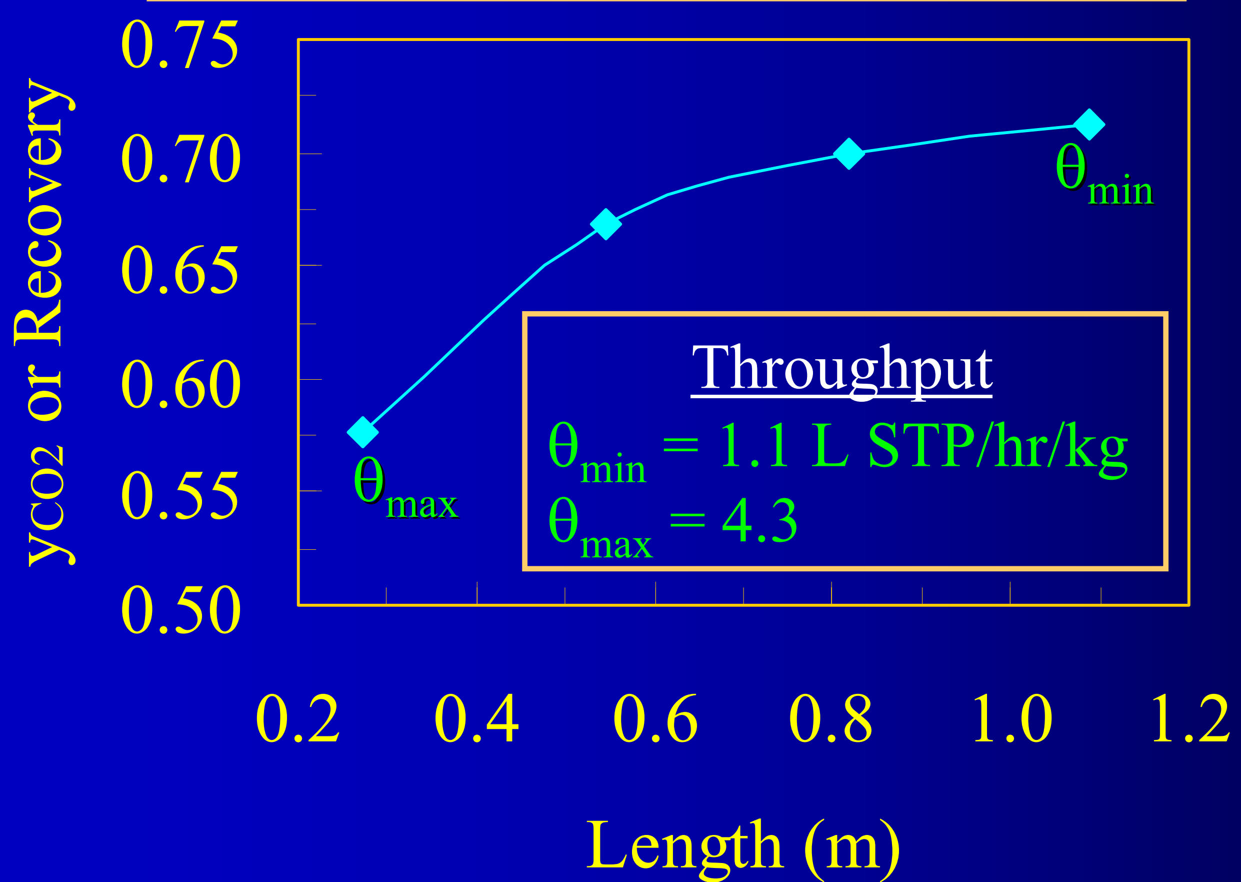
Operating Conditions

$y_{CO2} = 0.15 \quad y_{H2O} = 0.10 \quad y_{N2} = 0.75$

$P_H = 137.9$ kPa $\quad P_L = 13.79$ kPa

$t_{F/P} = t_{Pr/Bl} = 30$ s

$Q_F = 0.3$ L STP/min $\quad Q_{HP} = 0.15Q_F$



Enrichment of CO_2 in ER PSA easily surpasses that obtained with SR PSA, but typically at a much lower throughput and CO_2 recovery.

ER PSA: Effect of P_H

Operating Conditions

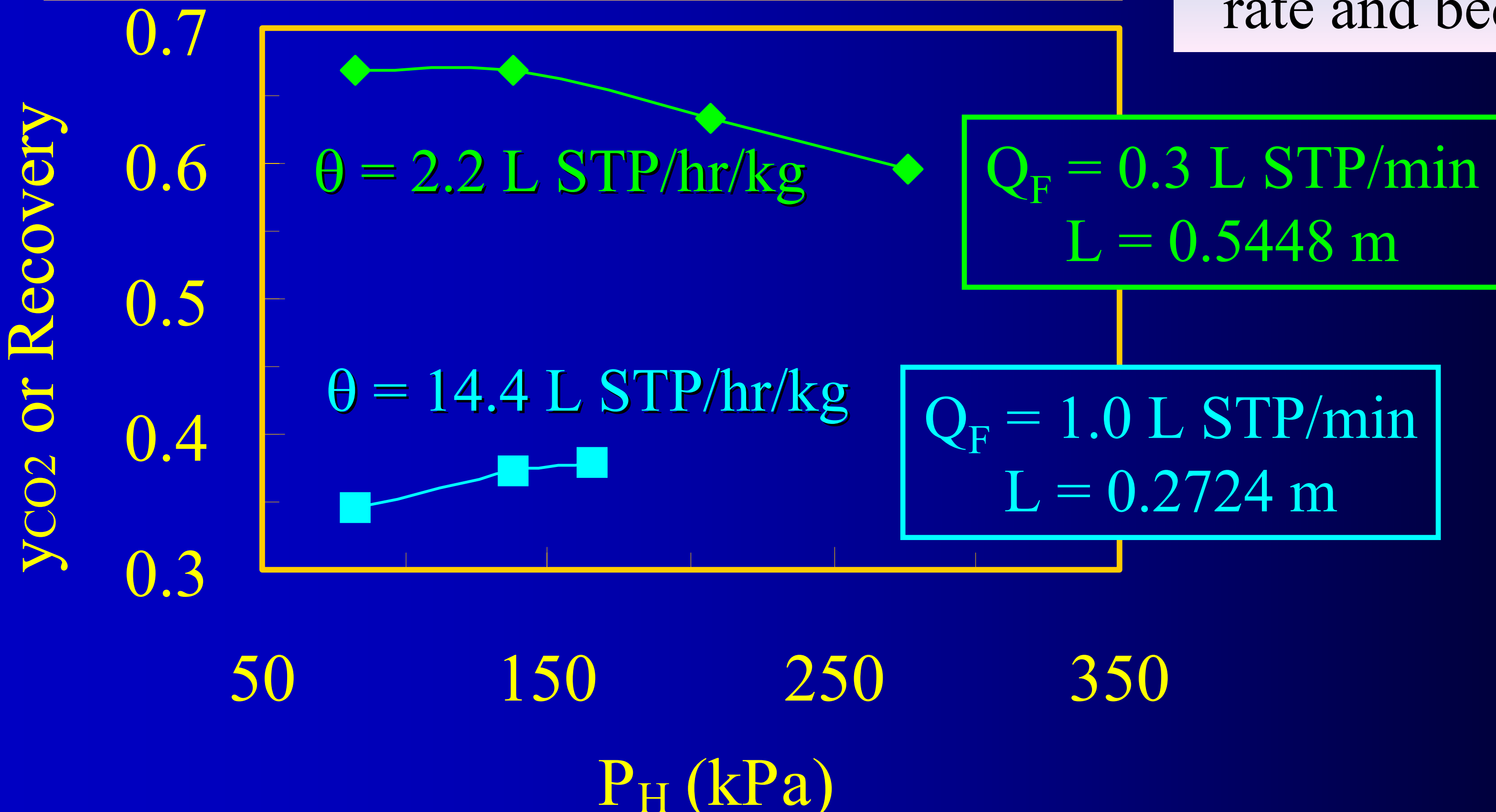
$y_{F,CO2} = 0.15$ $y_{F,H2O} = 0.1$ $y_{F,N2} = 0.75$

$P_L = 13.79$ kPa

$t_{F/P} = t_{Pr/Bl} = 30$ s

$Q_{HP} = 0.15 Q_F$

Interesting opposing effects of P_H, depending in some way on the feed flow rate and bed length.



ER PSA: Effect of $t_{F/P}$

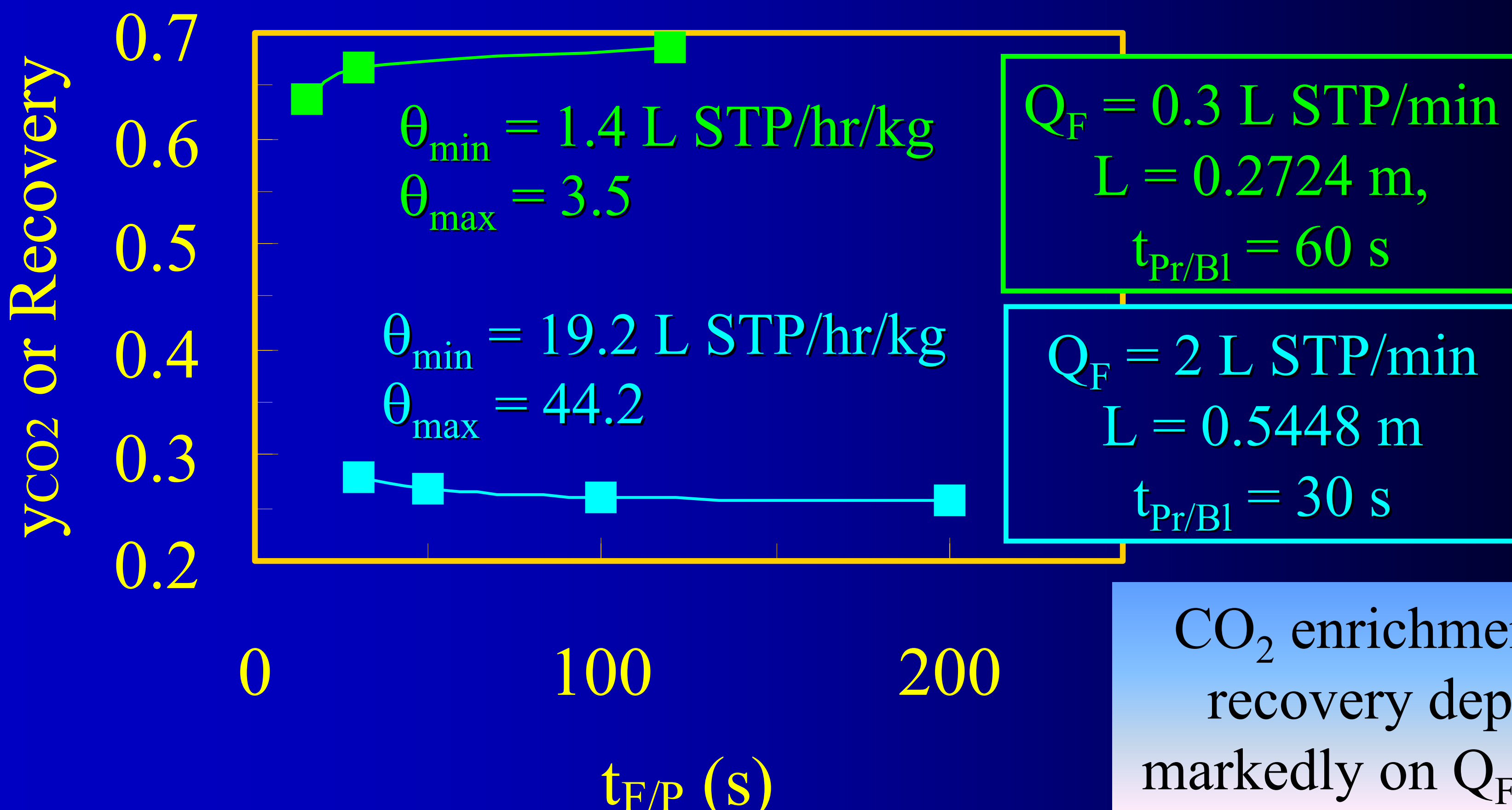
<u>Operating Conditions</u>

$y_{F,CO2} = 0.15$ $y_{F,H2O} = 0.1$ $y_{F,N2} = 0.75$

$P_H = 137.9$ kPa $P_L = 13.79$ kPa

$Q_{HP} = 0.15Q_F$

CO_2 enrichment and recovery relatively insensitive to $t_{F/P}$ at these conditions.



CO_2 enrichment and recovery depends markedly on Q_F and L!

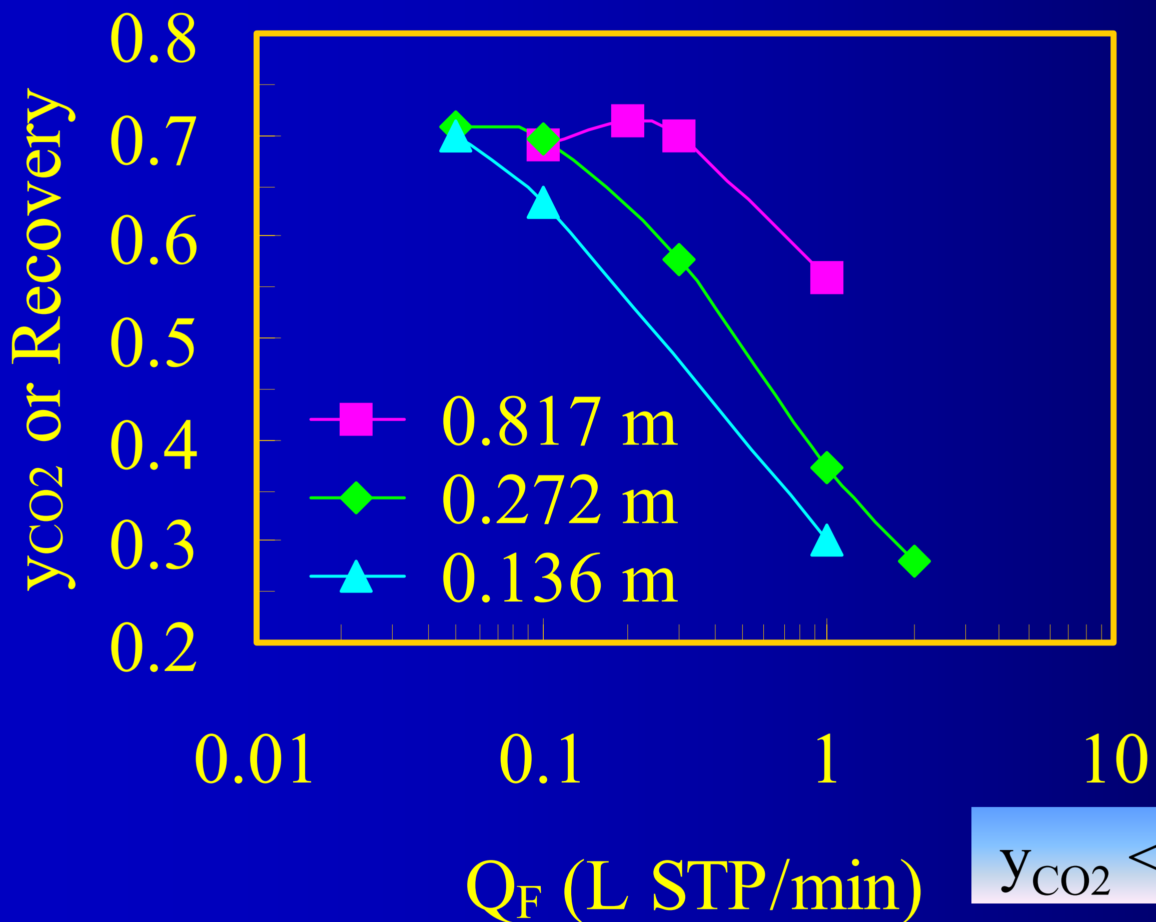
ER PSA: Effect of Q_F

<u>Operating Conditions</u>

$y_{F,CO2} = 0.15$ $y_{F,H2O} = 0.10$ $y_{F,N2} = 0.75$

$P_H = 137.9$ kPa $P_L = 13.79$ kPa

$t_{F/P} = t_{Pr/Bl} = 30$ s $Q_{HP} = 0.15Q_F$



<u>L = 0.817 m</u>

θ (L STP/hr/kg)

$\theta_{min} = 0.48$

$\theta_{max} = 4.8$

<u>L = 0.272m</u>

θ (L STP/hr/kg)

$\theta_{min} = 0.72$

$\theta_{max} = 28.8$

<u>L = 0.136 m</u>

θ (L STP/hr/kg)

$\theta_{min} = 1.4$

$\theta_{max} = 24.1$

$y_{CO2} < 0.75$ or $E_R < 5.0$ the limit?

Overall Objectives

- Propose why adsorption technology still has potential for CO_2 separation and capture
- Introduce new adsorption cycle concepts that mimic distillation technology
- Introduce new adsorbent material for reversible CO_2 adsorption at high temperature
- Describe high temperature adsorption cycles for concentrating CO_2 from stack and flue gases
- Provide convincing evidence that further justifies study of high temperature adsorption cycles

Comparison of ER and SR PSA Cycles

$\pi_T = 10$, $P_L = 13.79$ kPa, $L_b = 0.2724$ m

ER PSA
$Q_{HP}/Q_F = 0.15$

SR PSA
$\gamma = 0.5$

SR PSA
$\gamma = 1.25$

Flowrate (slpm)	Feed time (s)	θ (SLPH/kg)	Enrichment	Recovery (%)
0.050	30	0.72	4.71	70.0
0.100	30	1.44	4.65	69.9
0.300	30	4.32	3.85	50.1
1.000	30	14.40	2.48	37.4
2.000	30	28.81	1.87	28.2
0.250	100	3.60	0.99	100.0
0.500	100	7.20	1.63	100.0
1.000	100	14.40	2.42	96.8
1.500	100	21.60	2.69	81.9
2.000	100	28.80	2.78	69.4
0.250	200	3.60	1.64	100.0
0.500	200	7.20	2.45	100.0
1.000	200	14.40	3.13	89.3
1.500	200	21.60	3.28	73.8
2.000	200	28.80	3.29	62.6
0.250	100	3.60	0.94	100.0
0.500	100	7.20	1.46	100.0
1.000	100	14.40	2.09	100.0
1.500	100	21.60	2.37	94.8
1.750	100	25.20	2.42	89.3
0.250	200	3.60	1.48	100.0
0.500	200	7.20	2.08	100.0
1.000	200	14.40	2.64	99.5
1.500	200	21.60	2.77	89.5
1.750	200	25.20	2.76	83.6

Conclusions

- Simple 4 and 5 step SR PSA cycles are able to produce enriched CO_2 (but $y_{HP}/y_F < 4.0$) with very high recovery (100%) in a high temperature HTlc based process, <u>even with poor mass transfer characteristics which will improve</u>
- Simple 4 step ER PSA cycle is able to produce enriched CO_2 (but $y_{HP}/y_F < 5.0$) with with moderate recovery ($E_R < 80\%$) in a high temperature HTlc based process, <u>but at relatively low throughputs compared to SR PSA</u>
- Initial ideal and rigorous simulations of SR and ER PSA cycles providing considerable insight into which parameters appear to be most important to maximizing the CO_2 enrichment, recovery and throughput, <u>with upper thermodynamic limits being exposed</u>

Publications

- Steven P. Reynolds, Armin D. Ebner and James A. Ritter, "New Pressure Swing Adsorption Cycles for Carbon Dioxide Sequestration," Adsorption, submitted May 2004.
- Armin D. Ebner and James A. Ritter, "Equilibrium Theory Analysis of Stripping and Enriching Reflux Pressure Swing Adsorption Cycles for Carbon Dioxide Separation at High Tempertature," Ind. Eng. Chem. Res., submitted May 2004.
- Nick D. Hutson, Scott A. Speakman and E. Andrew Payzant, "Structural Effects on the High Temperature Adsorption of CO_2 on a Synthetic Hydrotalcite," *Chemistry of Materials*, submitted April 2004.

Many more manuscripts forthcoming!

Presentations

- S. P. Reynolds, A. D. Ebner and J. A. Ritter, "New Pressure Swing Adsorption Cycles for CO_2 Sequestration," 8th International Conference of Fundamentals of Adsorption (FOA8), Sedona, AR, May 2004.
- N. D. Hutson, S. A. Gadre, A. D. Ebner and J. A. Ritter, "Separation and Capture of CO_2 using a High Temperature Pressure Swing Adsorption System," Third Annual Conference of Carbon Capture & Sequestration, Alexandria, VA, May 2004.
- J. A. McIntyre, N. D. Hutson, A. D. Ebner and J. A. Ritter, "New Adsorption Technology for CO_2 Sequestration," AIChE 2003 Annual Meeting, San Francisco, CA, November 2003
- J. A. McIntyre, N. D. Hutson, A. D. Ebner and J. A. Ritter, "New Adsorption Technology for CO_2 Sequestration," 13th Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, Tennessee, October 2003.

Two more to give later this year, one invited!

Supported Students and Researchers

- Steven P. Reynolds, PhD student: supported through NSF K-12 Graduate Fellowship; working with Sarang on SR, ER and DR PSA code development, and design of high temperature PSA system to be built with continued funding
- Sarang A. Gadre, Postdoctoral Associate: supported partially by this grant and MeadWestvaco Fellowship; working with Steven on PSR code development, in particular on the DR PSA code
- James A. McIntyre, PhD, May 2003: supported by Mead-Westvaco Fellowship; after defending PhD, stayed on for 3 months and initiated ER and DR PSA computer code development for the high temperature adsorption cycles
- Armin D. Ebner, Research Assistant Professor: supported partially by this grant and MeadWestvaco Fellowship; working equilibrium theory SR, ER and DR PSR code

Overall Objectives

- Propose why adsorption technology still has potential for CO_2 separation and capture
- Introduce new adsorption cycle concepts that mimic distillation technology
- Introduce new adsorbent material for reversible CO_2 adsorption at high temperature
- Describe high temperature adsorption cycles for concentrating CO_2 from stack and flue gases
- Provide convincing evidence that further justifies study of high temperature adsorption cycles
- Elaborate on industrial and government agency collaborations to strengthen possibility of success

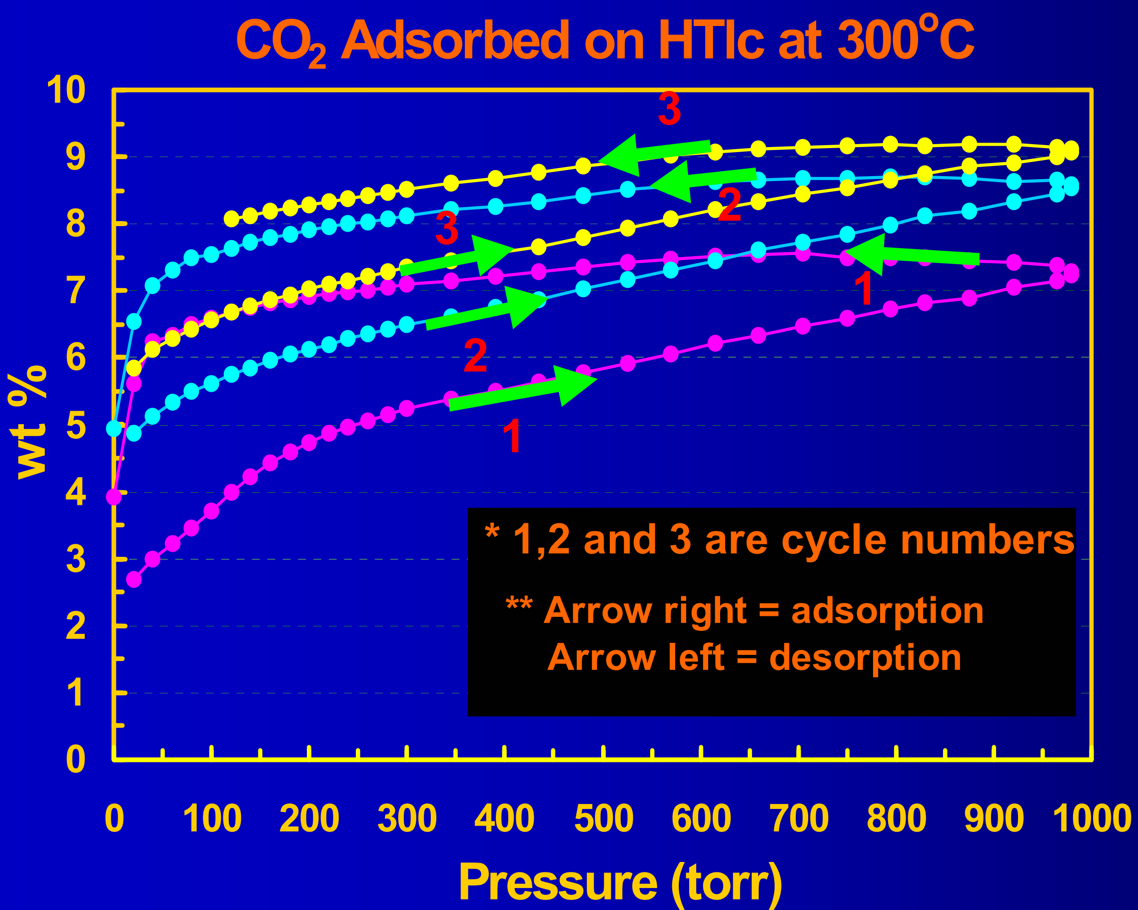
Collaborators

- University of South Carolina
  - new high temperature PSA adsorption cycles and adsorbent characterization
- Air Products
  - technical support, and product and process development and licensing
- US EPA Office of Research and Development
  - adsorbent development, characterization, and optimization

Preliminary Cycling Study with New EPA Material

$Mg_{0.73}Al_{0.27}(OH)_2](CO_3)_{0.135} \bullet mH_2O$

(with trace $NaNO_3$ impurity)



- **Adsorption isotherms with strong hysteresis (results consistent with observations of Ding and Alpay)**
- **Hysteresis loop continually displaced upwards, but less in every new cycle ⇒ regeneration approaching 100% in few more cycles (PSA cycles > 1000!!)**
- **Anyhow, working capacity tends to be larger than 3 wt%, which is quite remarkable**

On-Going and Future Research

- Continue to explore SR, ER and DR PSA cycles using the NLIET models to gain an understanding of the upper thermodynamic limits of performance
- Continue to develop NI-MTL SR, ER and DR PSA process simulator codes to explore new cycles under realistic conditions, e.g., high pressure rinse step in SR PSA compared to heavy reflux in ER and DR PSA
- Continue to collaborate with Nick Hutson at the EPA and Jeff Hufton at Air Products to foster the development of high temperature PSA cycles based on HTlc adsorbents for CO2 separation and capture
- Continue to characterize new and commercially available HTlc materials to determine more accurately their thermodynamic and transport properties, and initiate the design of a high temperature, universal SR, ER and DR PSA apparatus

Acknowledgements

Funding provided by DOE NETL, MeadWestvaco and Separations Research Program at the University of Texas at Austin is greatly appreciated!

Thank You!